A Practical Course in Chemical Technology

Edited
by
I. P. Mukhlyonov

Практикум по общей химической технологии

под редакцией
проф. И. П. Мухленова

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TO THE READER

Mir Publishers would be grateful for **your comments** on the content, translation and **design of this book**. We would also be pleased to receive **any other suggestions** you may wish to make.
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Preface

The course in chemical technology taught at chemical colleges and departments consists of three parts: lectures, practical studies, and laboratory works. A combination of these three teaching methods provides students with a sound foundation for studying any discipline of chemical technology.

This course is aimed primarily at presenting the basic laws of chemical technology, applicable to most chemical processes as well as processes of the metallurgical, silicate, pulp-and-paper and fuel processing industries. Studying the basic types of chemical processes—homogeneous and heterogeneous, noncatalytic and catalytic, electrochemical—and the associated reactors is combined with analysis of concrete processes of the greatest importance for the national economy. Particular attention is given to typical processes embodying the major aspects of chemical technology. The lectures and laboratory works also cover the structural materials used in the manufacture of chemical reactors.

In the 3rd Russian edition, emphasis is placed on analysis of automated and computerized reactors, as well as new methods and instruments employed in the investigation of material properties. Thus, students performing a laboratory work better assimilate the facts presented in lectures, acquire skills for controlling industrial processes with the aid of advanced instrumentation and computers, learn analytical procedures, and improve their techniques of processing the experimental results.

In a laboratory, students carry out the first (according to the syllabus) experiment. Each work covers practically all stages of experimental procedures. First of all, students learn about the subject from the textbook in chemical technology, the present practical course, and the literature recommended at the end of each work. Then, they go through the safety rules to be observed in a chemical labo-

ratory (see Appendix, p. 425) and the instructions to the work being carried out. After a briefing by the instructor (colloquium), students are assigned to conduct the experiment. Students then become familiar with the experimental setup, check whether it is assembled correctly, activate individual units, and calibrate some instruments.

The next stage is an experimental study of the effect of some process parameters on the course of the process. Some assignments involve analysis of the effect of temperature, concentrations, time, and other factors within a broad range so as to enable students to plot the process characteristics as a function of a particular variable.

Students make the necessary calculations using the experimental results and write a report including the statement of the problem and purpose of the work, process flow sheet calculations and plots based on the experimental results, and conclusions. An assignment must be stated in such a manner as to enable students to complete the experiment within six hours. Every student must carry out laboratory works from all six chapters, while particular assignments are given depending on his or her specialization.

Most of the works included in the 3rd Russian edition have been presented by the Lensovet Technological Institute in Leningrad. Other contributors include the Kuybyshev Polytechnic Institute (Work 16), Kazan Institute of Chemical Technology (Work 20), and the D. I. Mendeleyev Institute of Chemical Technology in Moscow (Work 25).

The introductions to all works have been written by I. P. Mukhlyonov. Works 1, 2, 5, 10, and 14 have been written by E. S. Tumarkina; Works 4, 7, 8, 9, 11, 12, 18, 19, 28, and 36 by A. Ya. Averbukh; Works 17 and 27 by B. A. Kopylev; Works 6, 15, 29, 30, and 31 by E. S. Rumyantseva; Work 33 by N. P. Matveyeva; Work 34 by E. A. Vlasov; and Works 35 and 37 by G. V. Cherepkov.

The authors will be grateful to all those who will send their critical comments and suggestions concerning the practical course.

Chapter 1

Noncatalytic Processes

In general chemical technology, systems and processes are classified in accordance with the phase state of the reacting substances since it determines the selection of processing techniques and design of the reactors. All interacting systems and the corresponding processes are divided into homogeneous and heterogeneous ones. The homogeneous systems are characterized by all interacting substances being in a single phase — gas (G) or liquid (L). The heterogeneous systems comprise at least two phases*. The following may be the types of two-phase systems: gas-liquid (G-L), gas-solid (G-S), two immiscible liquids (L-L), liquid-solid (L-S), and two solid phases (S-S). The systems most commonly used in the industry are L-S, G-L, and G-S. In many cases, industrial processes involve three or four phases, for example, G-L-S, G-S-S, G-L-S-S, and so on. Solid mineral stock almost invariably includes several phases for each mineral is essentially equivalent to an individual phase. In general, however, only the basic minerals are considered as individual phases, while the numerous impurities are disregarded.

In some cases, all solid materials interacting with other portions of a system are considered, for simplicity, as a single solid phase, while the liquid emulsion consisting of two or more phases is regarded as just one liquid phase, and the system is referred to as L-S although it essentially comprises two liquid and several solid phases. The L-L and L-S systems normally include a gas phase stemming from the fact that liquids and many solids undergo some degree of evaporation. However, the resulting gas (vapour) phase is taken into account, provided it plays a significant role in the interaction. As a general rule, only those substances and process parameters are taken into account in the analysis and development of processes, whose influence on the latter is decisive.

The laboratory works presented in this manual cover processes with different combinations of phases in two- and polyphase systems. Some of the processes are initiated in a homogeneous liquid

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* A group of substances involved in a physical or chemical interaction is referred to as a system. A phase is the totality of homogeneous portions of a system, having identical composition as well as physical and chemical properties and separated from other portions of the system by a definable boundary.

system which then becomes heterogeneous as a result of emergence of a new liquid (Works 4 and 17), solid (Works 2 and 9), or gas (Works 1 and 26) phase. In the processes of solid fuel pyrolysis and decomposition of limestone (Works 6, 7, and 8), the starting material is solid with a gas phase appearing at the end of the process. In other cases, a process initially involves a two-phase system, then yields a product in the form of a third phase (Work 2). Sometimes, a plurality of products in the form of different phases are yielded (Works 1, 18, and 30).

An *industrial chemical process* comprises the following interrelated unit processes (steps): (1) transfer of the reacting substances into the reaction zone, (2) chemical reactions, and (3) removal of the products from the reaction zone.

The *transfer of the reacting substances* into the reaction zone in homogeneous systems as well as within each liquid or gas phase of a heterogeneous system is by way of molecular diffusion or convection. The heterogeneous systems additionally involve the step of transition of a reacting substance from one phase to another, which occurs through absorption, adsorption or desorption of gases, condensation of vapours or evaporation of liquids, melting of solids or their dissolution in liquids. The phase change is in most cases the slowest step of a process and determines its overall rate. It is essentially a complex diffusion process.

The *chemical reactions* occur between the basic reagents, between the basic reagents and impurities, as well as between impurities. Several consecutive (or, in some cases, simultaneous) reactions may yield the same product. Main and by-products are formed in a process. Since the feed stock always contains various impurities, speaking strictly in chemical terms one may assume that a process involves a great number of reactions. However, in practice, account is taken of only one or several reactions yielding a sizable amount of main and by-products.

The *removal of products* from the reaction zone is also by way of molecular diffusion, convection, and phase change, just as in the case of their transfer into the latter. The product is often removed through condensation or absorption from a gaseous reaction mixture and through precipitation or desorption from a liquid one.

Processes and the associated reactors are also classified according to some of the operating conditions. Such a classification implies, primarily, batch processes and continuous ones conducted in flow reactors. As far as the degree of mixing of the reaction masses is concerned, processes and reactors belong to the following categories in terms of the limiting cases: plug-flow, perfect-mixing, and partial-mixing ones. Classification according to temperature conditions includes isothermal, adiabatic, and polythermal flow reactors and processes conducted in the latter.

According to reaction types, processes are divided into simple (Works, 1, 3, and 13) and complex ones that may involve consecutive and parallel reactions (Works 2, 14 and 18). Processes are also known to be reversible and irreversible, the latter being unidirectional. Depending on the actual conditions, reversible processes may be forward or backward. Irreversible processes are observed in the decomposition of natural phosphates by acids, as well as in polymerization and polycondensation. Typical irreversible processes also include fuel pyrolysis, roasting of raw sulphides, and some others covered in the laboratory works. Reversible processes include causticization of soda solution, the phase changes and reactions involved in the carbonization of ammoniacal brine, oxidation of sulphur dioxide, and others.

The *equilibrium in processes* corresponds to equality of the rates of the forward and backward processes, which results in the system component ratio remaining invariable until changes occur in the process conditions. Changes in such process parameters as temperature, pressure, and concentration of the reacting substances upset the equilibrium of a system, thereby bringing about spontaneous chemical reactions and diffusion processes in the system with the result that its equilibrium is restored. The effect of the basic process parameters on equilibrium is determined by Le Chatelier's principle stating that if a system in an equilibrium state is disturbed, it will readjust itself so as to minimize the disturbance and restore the equilibrium.

A quantitative measure of mobile equilibrium is the chemical reaction equilibrium constant for all homogeneous and heterogeneous processes occurring in the kinetic region. For example, in the case of processes in which the percentage conversion is determined by the equilibrium of the reaction

$$m\text{A} + n\text{B} \rightleftarrows p\text{D},$$

the equilibrium constant K is determined from the following equation:

$$K = \frac{[\text{D}^*]^p}{[\text{A}^*]^m \, [\text{B}^*]^n} \tag{1.1}$$

where $[\text{D}^*]$, $[\text{A}^*]$ and $[\text{B}^*]$ are the equilibrium concentrations of the reacting substances. In chemical-engineering studies Eq. (1.1) is often simplified.

The equilibrium of heterogeneous processes in the diffusion region is qualitatively defined by the Le Chatelier principle, whereas in quantitative terms it is defined by the distribution law establishing a constant ratio between the equilibrium concentrations of a component in different phases of a system at constant temperature and pressure. When applied to G-L systems, the distribution law is re-

ferred to as Henry's law:

$$p = \psi C_1^* \tag{1.2}$$

where p is the equilibrium partial pressure of the component absorbed in the gas, ψ is the Henry's law constant having the dimension of pressure, and C_1^* is the mole fraction of the component absorbed in the solution.

The phase equilibrium in two- and polyphase systems is governed by the phase rule

$$F = 2 + C - P, \tag{1.3}$$

where F is the number of degrees of freedom, or variance, of a system, C is the number of individual chemical components in the system, P is the number of phases, and 2 is the number of external factors affecting the phase equilibrium. As a rule, the external factors include temperature and pressure. In some cases, pressure is ignored and instead of 2 we have 1 (e.g. when the effect of pressure variations is insignificant).

Experimental or calculation data are used to plot, on the basis of the phase rule, phase diagrams in which a particular property of a system, such as melting or boiling point, is determined as a function of composition.

The *process rate* is the resultant of the rates of the forward, back, and side reactions plus those of the convection and diffusion of the starting substances into the reaction zone and of products from the latter. If the reaction rate is less than that of the diffusion processes involved in the introduction of the reacting substances and removal of the products, then the process is said to occur in the kinetic region, and, in order to speed it up, one must raise the temperature, increase the reagent concentration, and use catalysts. The kinetic region is where most homogeneous processes take place. If the reaction rate exceeds by far the rate of the diffusion processes, the overall rate is determined by diffusion (the process occurs in the diffusion region). Such a process can be accelerated primarily by mixing the reacting substances and controlling pressure. The use of a catalyst does not make the diffusion faster. Many heterogeneous processes are associated with the diffusion region. If the rates of the reactions and diffusion processes are commensurate and the process is observed in a region intermediate between the kinetic and diffusion ones, one should first of all resort to the factors that speed up both the reactions and the diffusion at a time, that is increase the temperature and concentrations.

The rate of a process is calculated on the basis of the product yield within a time interval or the process rate constant (coefficient).

The first kinetic characteristic of a process, which is calculated from experimental data, is the product yield. The product yield x

is defined as the ratio of the actual amount of the obtained product (G_a) to the maximum amount that could be obtained from the starting substances (G_{max}):

$$x = G_a/G_{max}. \qquad (1.4)$$

The maximum product amount G_{max} is calculated for chemical reactions, at a stoichiometric ratio of the starting substances (e.g. in ammonia synthesis), as a sum of the amounts of the starting substances that could enter into the reaction (in accordance with the reaction equation). For example, in the case of the reaction

$$m\text{A} + n\text{B} \rightleftharpoons p\text{D},$$

the maximum amount of the product D is

$$G_{max} = G_A + G_B. \qquad (1.5)$$

In practice, the starting substances usually are not in a stoichiometric ratio. Then, the yield is calculated from the main (most valuable) starting substance. For instance, when the atmospheric oxygen is used to oxidize sulphur dioxide to sulphur trioxide, ammonia to nitrogen oxide, methanol to formaldehyde, or ethylene to ethylene oxide, the yield is calculated without taking oxygen into account, that is G_{max} is determined with respect to the end product amount that would be derived as a result of complete conversion of SO_2, CH_3OH, and $CH_2 = CH_2$, respectively. For example, in the case of oxidation of SO_2 to SO_3, G_{max} in the final mixture at the reactor exit will be

$$G_{max} = G_{SO_3} + G_{SO_2}. \qquad (1.6)$$

Similarly, the amount of water spent in hydration, hydrolysis, and other such processes is not taken into account either.

In Eq. (1.5), the amounts G of the substances can be substituted by their concentrations C_f in the final mixture having a definite (measured) volume v in view of the fact that $G = Cv$. For example, the yield of the sulphur trioxide resulting from oxidation of sulphur dioxide is determined from the equation

$$x = C_{fSO_3}/(C_{fSO_3} + C_{fSO_2}). \qquad (1.7)$$

If the maximum amount of the product of a chemical reaction is assumed to equal the amount that would be obtained in accordance with the equation of the reaction (disregarding the equilibrium conditions), the yield is referred to as percentage conversion. The percentage conversion of the main starting substance can be determined from the equation

$$x = (G_i - G_f)/G_i = (C_i - C_f\beta)/C_i, \qquad (1.8)$$

where G_1 and G_f are the initial and final amounts of the main starting substance, C_1 and C_f are its initial and final concentrations, and β is a factor of conversion of the final concentration with respect to the initial one, the factor β takes into account changes in volume as a result of the reaction (synthesis or decomposition) as well as temperature and pressure fluctuations.

In mass-transfer processes, the yield defined by Eqs. (1.4) and (1.8) is called the degree of phase-to-phase transfer or, more specifically, the degree of absorption, desorption, and so on. In this case, the maximum amount of the product is assumed to be that present in the donating phase such as gas during absorption. The percentage conversion of irreversible processes tends to unity in the course of time while that of reversible processes is always less than unity.

As far as reversible processes are concerned, two more definitions are associated with the product yield. The theoretical or equilibrium yield (x_{eq}) is the ratio of the amount of the product at equilibrium (G_{eq}) to the maximum possible amount that is

$$x_{eq} = G_{eq}/G_{max}. \tag{1.9}$$

The yield as percentage of the theory (x_a) is the ratio of the actually derived amount of the product to that expected at equilibrium, that is

$$x_a = G_a/G_{eq} = G_a/G_{max}x_{eq}. \tag{1.10}$$

In Eqs. (1.9) and (1.10) just as in Eq. (1.4) G_{max} can be expressed as the sum of the amounts of the starting substances G_A and G_B. In the case of homogeneous media, the amouts of substances can be substituted by their final concentrations (cf. Eqs. (1.7) and (1.8)). The product yield x may be dependent on many parameters and even in the case of hydrodynamic similarity it is expressed a complex function which can be written, for the reaction

$$m\text{A} + n\text{B} \rightleftharpoons p\text{D}$$

as follows:

$$x = f\,(\tau,\ t,\ P,\ C_A,\ C_B). \tag{1.11}$$

Proceeding from expression (1.11), the dependence of the product yield on any parameter, such as temperature t, in all laboratory works must be determined with all the other process parameters included in this expression being constant, that is measurements should be taken and analyses made at different temperatures but after the same time interval τ has elapsed from the onset of the reaction, at the same starting substance concentrations, and at a constant pressure P. In addition, to maintain the hydrodynamic conditions constant, all experiments should be carried out using the same experimental setup (or geometrically similar setups), at

constant flow rates of the reaction masses, at a constant ratio between the volumes of the interacting phases (S : L = const, S : G = const, L : G = const, etc.), and under constant mixing conditions. Should one of these conditions not be met, then, in comparing the experimental results, for example, in plotting the yield-versus-temperature curve, one must introduce correction factors derived from other experiments or calculations.

Typical curves showing the dependence of the product yield on the basic process parameters with all the other experimental conditions
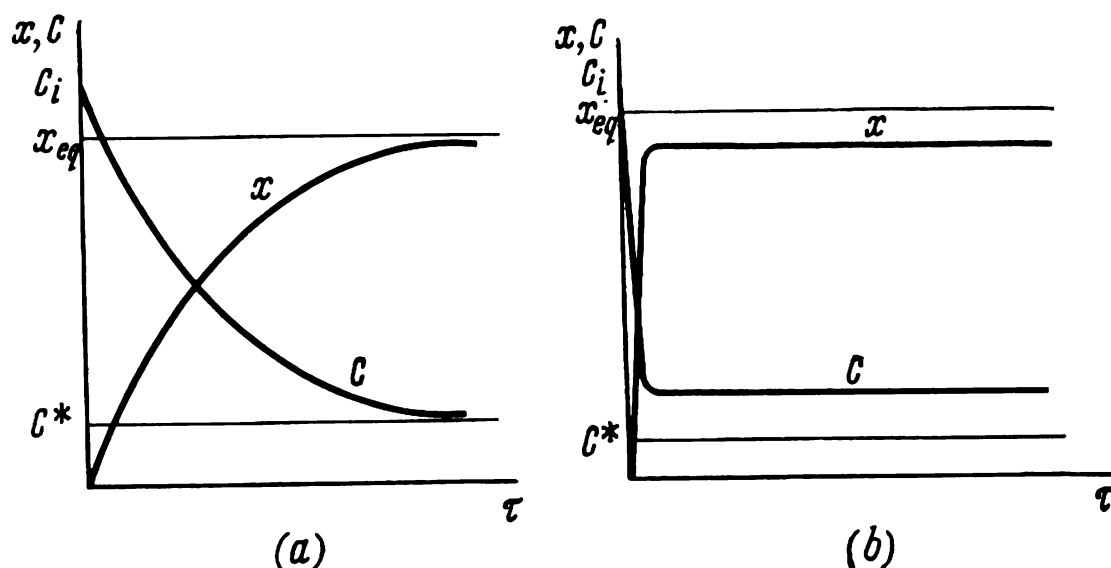
Fig. 1. Product yield x and main starting substance concentration C versus reagent residence time τ:

a—in plug-flow reactor; *b*—in perfectly mixed reactor

being invariable are presented in Figs. 1 through 5; whatever departures from these curves arise while the experimental data are processed in the laboratory works should be explained in the reports (the factors causing these departures must be mentioned). Fig. 1 represents the kinetics of a chemical process (a) in batch (non-flow) reactors and plug-flow reactors in which the starting reagents are not mixed with the reaction products and (b) in continuous reactors with perfect mixing of the reagents with the reaction products.

In batch and plug-flow processes, the equilibrium (C^* and x_{eq}) is attained sooner than in processes involving mixing, however, processes with mixing under isothermal conditions lead to an increase in x_{eq} and a decrease in the equilibrium concentration C^* of the starting substance, as compared to the adiabatic conditions typical of plug-flow reactors. The plug-flow and perfect-mixing conditions are extreme. The x and C curves for real processes occupy an intermediate position between the plug-flow and mixing curves (Fig. 1*a*, *b*,).

The closest one can get to the plug-flow conditions is in apparatus for homogeneous processes involving gases, packed towers, and reactors with a solid filter bed, particularly shaft furnaces and converters. The perfect-mixing conditions are best attained in stirred liquid reactors, bubble columns and froth apparatus, as well as fluidized-bed reactors.
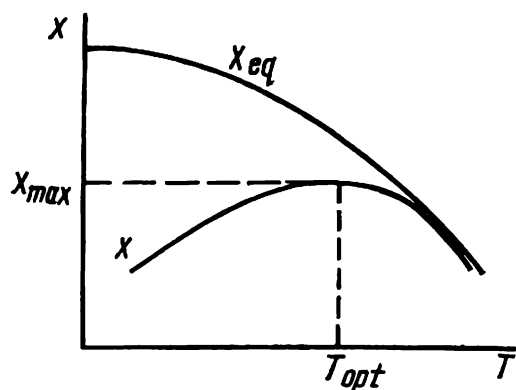
Fig. 2. Effect of temperature on conversion x and equilibrium yield x_{eq} in isothermal reversible reactions

Raising the temperature of an exothermic process brings the system to equilibrium much sooner but the equilibrium shifts toward the starting substances. As a result, the product yield increases with temperature at a point far from the state of equilibrium, reaches the maximum at an optimal temperature, then decreases as the temperature continues to rise (Fig. 2).

When the temperature of an endothermic process is raised, the product yield increases monotonically to a certain limit depending on the nature of the reacting substances (Fig. 3).

Increasing pressure (Fig. 4) in gas reactions accompanied by a reduction of the gas mixture volume and in absorption or conden-
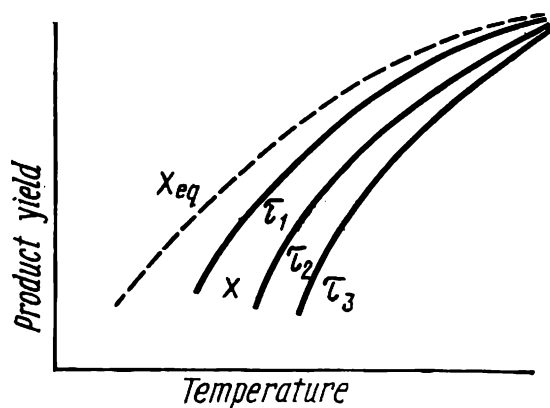
Fig. 3. Effect of temperature on equilibrium (x_{eq}) and actual (x) yields in endothermic reversible reactions at different reagent residence times: $\tau_1 > \tau_2 > \tau_3$
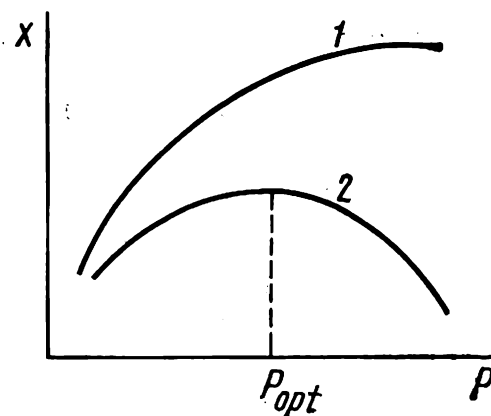
Fig. 4. Product yield versus pressure:

1—in processes with [decreasing volume $\Delta n < 0$; *2*—in processes with increasing volume $\Delta n > 0$

sation of gases and vapours leads to a continuous but gradually slowing increase in the product yield. When the volume of the gas mixture in such reactions expands, increasing pressure speeds up the process but the equilibrium shifts toward the starting substances (Le Chatelier's principle). In the latter case, the yield curve *2* passes

through a maximum. The optimal pressure for various processes varies widely from fractions to tens of atmospheres.

The effect of reagent concentrations on the product yield depends on the order of the chemical reaction. In mass-transfer processes unencumbered by chemical reactions and in first-order reactions the amount of the product grows in proportion to the starting substance concentration in the reaction volume; hence, the degree of conversion or transfer of a component from one phase to another is independent of the starting substance concentration. The $x = f(C)$ plot will feature a straight line parallel to the abscissa. When one of the reacting substances is in excess over the stoichiometric amount, the product yield with respect to the other will increase.

The effect of the reaction order on process rate variations in the course of time can be seen in the curves showing that the concentration of the main starting substance decreases (Fig. 5). The rate of the zero-order reaction (line 0) remains invariable in time. The higher the reaction order, the more pronounced the effect of the reagent concentration on the process rate.
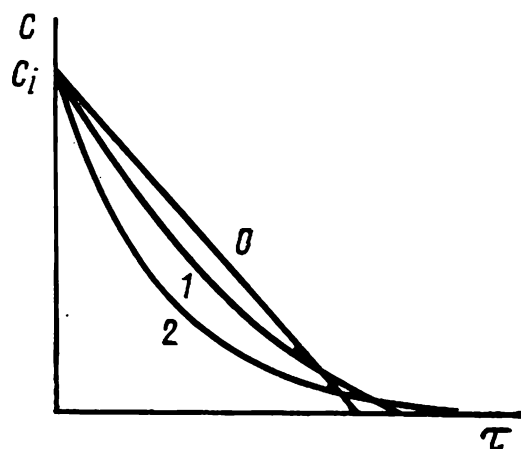
Fig. 5. Decrease in main starting substance concentration C over time τ in an irreversible reaction, depending on its order (0th, 1st, 2nd), under conditions close to plug flow

The process rate constant is independent of the reaction time τ and reagent concentrations C_A and C_B within certain limits, while its dependence on temperature t and pressure P can be easily calculated from known formulas. Consequently, the rate constant is the most convenient criterion for comparing and calculating the process rate under various conditions; it is included in the fundamental process rate formulas.

Basic Process Rate Equations. Kinetic equations may differ substantially depending on the degree of mixing of the reagents with the reaction products in the course of a process. Under conditions close to plug flow (see Fig. 1a), the reagent concentrations C decrease monotonically in time (or with increasing reactor volume) following a curve asymptotically approaching, at the end of the process, the equilibrium concentrations C^* of the starting substances. Accordingly, the overall process rate u is expressed in terms of differential equations:

(a) for homogeneous processes with the product concentration C_{pr} increasing over time τ:

$$u = dC_{pr}/d\tau = k\Delta C, \qquad (1.12)$$

where k is the process rate constant and ΔC is the driving force expressed as the product of the actual starting substance concentrations;

(b) for heterogeneous processes occurring in the diffusion region at a known interfacial area F,

$$u = dG_{pr}/d\tau = kF\Delta C, \qquad (1.13)$$

where G_{pr} is the amount of the reaction product, obtained within the time interval τ, and k is the process rate constant also known as the mass-transfer coefficient;

(c) for homogeneous and heterogeneous processes in the kinetic and diffusion regions:

$$u = dG_{pr}/d\tau = kv\Delta C \qquad (1.14)$$

or, with a variable reactor volume,

$$u = V_r dG_{pr}/dv = k\Delta C, \qquad (1.15)$$

v being the reaction volume and V_r being the volume of the reaction mixture passing through the reactor per unit time (gas, liquid, or solid flow rate). The process rate is often expressed in terms of variations in the percentage conversion or product yield x in time, then kinetic equation (1.12) takes the form

$$u = dx/d\tau = k\Delta C. \qquad (1.16)$$

Eqs. (1.12) through (1.16) are applicable to calculate the process rate in batch reactors operating under plug-flow and mixing conditions.

Under perfect-mixing conditions in flow reactors (see Fig. 1b) the concentrations of the main starting substance (C) and product (C_{pr}) as well as the product yield x are constant throughout the reactor volume and equal to the final quantities (at the reactor exit). Therefore, the reaction rate is expressed as the ratio of the final quantities (end product amount G or product concentration C_{pr} or conversion ratio x) to the reaction time τ or reactor volume v, rather than a differential. Thus, Eqs. (1.12) through (1.16) are written as follows:

$$C_{pr}/\tau = k\Delta C_f, \qquad (1.12a)$$

$$C_{pr}/\tau = kF\Delta C_f, \qquad (1.13a)$$

and so on, ΔC_f being the driving force corresponding to the final concentration of the reacting substances ($\Delta C_f = \text{const}$).

The process rate can also be expressed in terms of time variations of the amount $G_{s.s}$ or concentration $C_{s.s}$ of the main starting substance. Then, the expression for the process rate under plug-flow con-

ditions will be

$$u = - \frac{dG_{s.\,s}}{d\tau} \quad \text{or} \quad u = - \frac{dC_{s.\,s}}{d\tau}. \qquad (1.17)$$

The rate constant k in Eqs. (1.12) through (1.16) and in Eqs. (1.12a) and (1.13a) is a complex value dependent on the chemical and physical properties of the reacting substances, flow rates of the reaction masses, mixing of the components, and reactor design. In the case of hydrodynamically similar systems, k is, generally, a function of the rate constants k_1 (forward reaction), k_2 (back reaction), k_s' and k_s'' (side reactions), as well as coefficients of transfer (diffusion) of the starting substances into the reaction zone and the reaction products from the latter—D_1, D_2 and D_1' and D_2', respectively.

$$k = f(k_1,\ k_2,\ k_s',\ k_s'',\ \ldots,\ D_1,\ D_2,\ \ldots,\ D_1',\ D_2',\ \ldots). \qquad (1.18.)$$

Of all the quantities included in the above expression only those of interest are used in calculations, that is the coefficients having a minimum value and, therefore, slowing down the process rate. This is why in the kinetic region the diffusion coefficients are not taken into consideration, while in the diffusion region only they are taken into account. A great variety of formulas are used to calculate k. In most cases, the experimental value calculated on the basis of experimental data from kinetic equations (1.12) through (1.17) is taken. For example, from Eq. (1.13) we have

$$k = \frac{G}{\tau F \Delta C_{\mathrm{m}}}, \qquad (1.19)$$

where ΔC_{m} is the mean logarithmic driving force of the process.

If the product amount G is measured in grammes, time in hours, interfacial area F in square metres, and driving force ΔC_{m} of the process in grammes per cubic metre of the reaction mixture, k will be expressed in $g/m^2 \cdot h \cdot g/m^3$ or m/h, that is in the same terms as linear velocity. If the rate constant is calculated using Eqs. (1.12), (1.14), and (1.15), k will be expressed in terms of h^{-1} at the same dimensions of the determining values.

In industrial apparatus it is usually difficult to determine the actual area F of the interface between the interacting phases because of the vigorous agitation of the gas and liquid phases and polydispersity of the solid phase. In such cases, included in Eqs. (1.13) and (1.19) is an arbitrary interfacial area numerically equal to the cross-sectional area of the apparatus, the surface area of its trays or packing, and so on. Then, the effect of mixing on F is implied in the value of k, which is itself dependent on mixing (since mixing substitutes for slow molecular diffusion by convection).

As to processes in the kinetic region, ΔC is calculated as the product of the reagent concentrations, that is ΔC is determined by the

reaction order. Under conditions close to plug flow, the current driving force for the model reaction

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons p\mathrm{D}$$
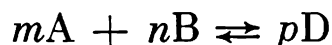
is calculated using the equation

$$\Delta C = (C_{\mathrm{A}} - C_{\mathrm{A}}^*)^m (C_{\mathrm{B}} - C_{\mathrm{B}}^*)^n. \tag{1.20}$$

If the total rate constant k is unknown and only the rate constants k_1 and k_2 of the forward and back reactions, respectively, are available, Eqs. (1.12), (1.15), and (1.16) take the form

$$u = k_1 \Delta C_1 - k_2 \Delta C_2, \tag{1.21}$$

where

$$\Delta C_1 = C_{\mathrm{A}}^m C_{\mathrm{B}}^n \quad \text{and} \quad \Delta C_2 = C_{\mathrm{D}}^p. \tag{1.22}$$

The current reagent concentrations cannot be used in calculations, therefore, the driving force is expressed in terms of the initial reagent concentrations and conversion of the reacting substances. Thus, the rate of an irreversible first-order reaction can be written as

$$u = dx/d\tau = k\Delta C = k\,(1 - x), \tag{1.23}$$

x being the conversion of the substance whose initial concentration is taken equal to unity. As can be seen from Fig. 1*a*, the concentration of the starting substance decreases, while x increases logarithmically, accordingly, Eq. (1.23) gives

$$k = \frac{1}{\tau} \ln \frac{1}{1-x}. \tag{1.24}$$

In the case of fractional-order reactions, which are predominant in practice, the kinetic equations used in calculations become highly complicated. For gas reactions, with due account for the effect of temperature and pressure, Eq. (1.16) takes the form

$$u = \frac{dx}{d\tau} = k_0 e^{-E/RT} \Delta C P^n, \tag{1.25}$$

where k_0 is the pre-exponential factor in the Arrhenius equation, e is the base of natural logarithms, E is the activation energy, R is the universal gas constant, T is thermodynamic temperature, ΔC is the driving force of the process at atmospheric pressure, P is dimensionless pressure in the reactor $(P/1)$, and n is the reaction order.

Under conditions close to complete mixing (see Fig. 1*b*) and Eqs. (1.12*a*), (1.13*a*) etc., the driving force is virtually invariable and equal to the final force ΔC_{f}:

$$\Delta C_{\mathrm{m}} = \Delta C_{\mathrm{f}} = \text{const.} \tag{1.26}$$

Similarly to Eq. (1.20) for a reversible reaction, we have

$$\Delta C_f = (C_{Af} - C_A^*)^m (C_{Af} - C_B^*)^n. \tag{1.20a}$$

For a first-order reaction the equation takes the form

$$u = \frac{x}{\tau} = k(1-x), \tag{1.27}$$

where the rate constant is

$$k = \frac{1}{\tau} \frac{x}{1-x}. \tag{1.28}$$

At any instant in mass transfer, the driving force equals the difference between the actual concentration of a component in the donating phase (C) and the concentration of the same component at equilibrium with the accepting phase (C^*):

$$\Delta C = C - C^*. \tag{1.29}$$

In the case of irreversible processes, such as chemisorption, the equilibrium concentration $C^* = 0$, and the driving force is equal to the concentration of the absorbed component in the donating phase. The driving force is expressed, for calculations, in terms of the initial and final concentrations of the transferred component, which are easy to measure at the inlet of a reactor and at its exit (during continuous operation) or at the beginning and end of the experiment*.

Under perfect-mixing conditions, the mean (calculated) driving force of mass transfer will be

$$\Delta C_m = \Delta C_f = C_f - C^*. \tag{1.30}$$

Under conditions of plug flow in each phase, that is without mixing or with slight mixing, ΔC_m is

$$\Delta C_m = \frac{\Delta C_1 - \Delta C_f}{2.3 \log (\Delta C_1 / \Delta C_f)}. \tag{1.31}$$

Controlling the Process Rate. The process rate, throughput of a reactor, and efficiency of its operation are determined by the three independent variables: k, F, and ΔC. The variables F and k are independent of the reagent concentrations, within certain limits, and, therefore, they may remain invariable throughout the process. In processes with slight mixing under conditions close to plug flow, the driving force decreases in the course of the process according to the

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* For logarithmic equations of the driving force of a process involving reversible mass transfer under conditions of co-current, counter-current and cross-current flows see *Chemical Technology* by I. Mukhlyonov, A. Averbukh, E. Tumarkina *et al.* Edited by I. Mukhlyonov, 3rd revised and expanded edition, Moscow, 1977, Part I, Chapter 2.

law of mass action along a die-away curve (Fig. 6). The process rate decreases along a similar curve in proportion to ΔC, hence, any process is difficult to bring to complete conversion of the starting substances to end products. The final steps, for example, from $x_a = 0.9$ to $x_a = 0.99$, usually take more time and require larger reactor volumes, as compared to x_a ranging from 0 to 0.9.

Analysis of Eqs. (1.12) through (1.16), (1.12a), and (1.13a) clearly indicates the measures to be taken in order to enhance the process rate. To increase the coefficient k in the kinetic region calls for higher temperature and catalysts, while to do the same in the diffusion region one must provide for more vigorous stirring and increase the temperature. Thus, raising the temperature is a universal means for speeding up processes, although it is restricted by equilibrium conditions, stability of the materials, economic and other factors.
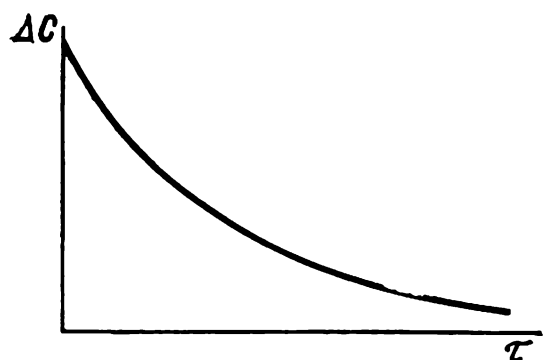
Fig. 6. Decrease in driving force of a process over its duration

In irreversible reactions (Works 5 through 9), the equilibrium does not affect heating. Therefore, to speed up the process and enhance the yield of the end product elevated temperatures are used, restricted primarily, by the heat resistance of the structural materials on the one hand and starting reagents and end products on the other. Application of pressure is most effective in processes involving volume reduction (gas-phase syntheses, absorption, etc.) and high reagent concentrations.

The interfacial area in heterogeneous systems is increased in different ways depending on the state of aggregation of the reacting substances. The laboratory works in general chemical technology cover the basic methods of developing the interfacial area. To increase the interfacial area in a G-S system use is made of finely divided materials or porous lumps in the filter or suspended (fluidized) bed. For a G-L system, bubbling, a suspended froth bed, and film mass transfer are used. L-S systems call for mechanical stirring, agitation by air, and conducting the reaction in the filter bed.

In homogeneous systems, lacking interfaces separating reagents from one another, the reactions are usually much faster than in heterogeneous ones, the entire process pattern is simpler, and control is easier. Therefore chemical engineers try to transform heterogeneous systems to homogeneous ones wherever possible. Reactions proceed at a particularly fast rate in the liquid phase, which is why it is often attempted to convert solid reagents to a liquid state

by melting or dissolving them; to the same end, gases are absorbed or condensed. These techniques will be encountered in some laboratory works.

The above regularities, of course, apply to all processes described in the chapters that follow. Accomplishment of the tasks outlined in all laboratory works will help students to assimilate the basics of practical chemical engineering and apply them to all processes that are currently in common use.

LABORATORY WORK 1. PRODUCTION OF PHOSPHORIC FERTILIZERS BY ACID DECOMPOSITION OF NATURAL PHOSPHATES

The processes involved in acid treatment of natural phosphates, such as apatites and phosphorites, typify heterogeneous noncatalytic processes in a polyphase L-S-G system, of which the limiting factors are the diffusion kinetics and phase-to-phase mass transfer. Acid decomposition of phosphates gives rise to a polyphase system comprising a liquid phase (solution), a number of new solid phases (gypsum, monocalcium phosphate, iron and aluminium phosphates, etc.), and a newly formed gas phase (hydrogen fluoride).

In contrast to many other heterogeneous processes occurring in L-G and G-S systems (catalysis, absorption, desorption, roasting, etc.), the production of mineral salts, in particular, phosphoric fertilizers, by acid decomposition of natural minerals is a complex multistep process which is extensive on the whole. This is due to the slow rates of individual steps of this heterogeneous process: diffusion of acids into the pores of the mineral particles, sometimes through the crust of newly formed crystals (transfer of the reagents into the reaction zone), as well as crystallization of the new solid phases, or salts, from the liquid phase (removal of the product from the reaction zone).

The most important of all phosphoric fertilizers are single and double superphosphates. Single superphosphate belongs to the relatively cheap versatile fertilizers widely used in agriculture. It is essentially a powder (or granulated material) containing water-soluble monocalcium phosphate $Ca(H_2PO_4)_2 \cdot H_2O$ in a mixture with calcium sulphate $CaSO_4$. Single superphosphate may contain 14 to 21% of P_2O_5 in the available form, depending on the quality of the raw material.

Double superphosphate is a high-analysis fertilizer and, unlike single superphosphate, it contains, mainly, monocalcium phosphate $Ca(H_2PO_4)_2 \cdot H_2O$ without calcium sulphate. It also contains a certain amount of iron and aluminium phosphates together with silica. The content of available P_2O_5 in double superphosphate ranges from

40 to 55% or, in other words, is two to three times higher than in single superphosphate. The double superphosphate containing 50 to 55% of P_2O_5 is also known as triple superphosphate.

The raw materials used in the production of single and double superphosphates are natural phosphates—apatites and phosphorites containing phosphorus in the form of insoluble solid salts, primarily fluorapatite $Ca_5F(PO_4)_3$ or hydroxyapatite $Ca_5OH(PO_4)_3$. The apatite concentrate resulting from flotation of the apatite-nepheline ore contains 39 to 40% of P_2O_5, phosphorites contain many impurities and even after flotation the content of P_2O_5 stays within 25 to 30%. The production of phosphoric fertilizers resides in processing of natural phosphates containing insoluble phosphorus salts that cannot be easily assimilated by plants into fertilizers containing phosphorus in a water-soluble or available (soluble in soil acids) form readily assimilated by plants.

Processing of Natural Phosphates into Single and Double Superphosphates. Single superphosphate is produced by subjecting apatites to decomposition by sulphuric acid. This is a heterogeneous process limited, primarily, by the diffusion kinetics and can be divided into two steps. The first step consists in diffusion of sulphuric acid toward apatite particles, accompanied by a rapid chemical reaction at the interface (apatite particle surface) till the acid is completely spent, as well as crystallization of calcium sulphate:

Fig. 7. Solubility isotherms in system $CaO-P_2O_5-H_2O$

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 2.5H_2O = 5(CaSO_4 \cdot 0.5H_2O) + 3H_3PO_4 + HF \quad (a)$$
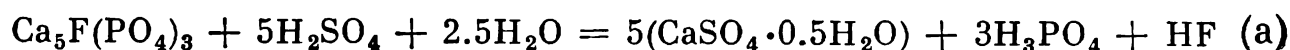
The second step is diffusion of the resulting phosphoric acid in the pores of the undecomposed phosphate particles, accompanied by the reaction

$$Ca_5F(PO_4)_3 + 7H_3PO_4 + 5H_2O = 5Ca(H_2PO_4)_2 \cdot H_2O + HF \quad (b)$$
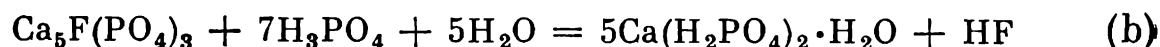
The resulting monocalcium phosphate initially stays in the solution, then starts to crystallize after the latter has been supersaturated. The diagram of equilibrium in the $CaO—P_2O_5—H_2O$ system (Fig. 7) suggests that at a P_2O_5 concentration of 42 to 46%

and a temperature above 100°C only monocalcium phosphate $Ca(H_2PO_4)_2 \cdot H_2O$ crystallizes from the solution.

The first step involving reaction (a) is completed in the superphosphate den within 30 to 60 minutes during setting of the superphosphate mass due to a relatively rapid crystallization of the poorly soluble calcium sulphate. The second step of the process—formation and crystallization of monocalcium phosphate—is much slower and over after the superphosphate has been in storage for 6 to 30 days The slow rate of this step results from the slow diffusion of phosphoric acid through the monocalcium phosphate crust formed in the process over the apatite grains and the extremely slow crystallization of the new solid phase $Ca(H_2PO_4)_2 \cdot H_2O$.

The optimal conditions in the reaction chamber are determined not only by the kinetics of the reactions and acid diffusion but also by the structure of the formed calcium sulphate crystals, which affects the overall process rate and superphosphate quality as well. The diffusion and reactions (a) and (b) can be sped up by increasing the sulphuric acid concentration and temperature. An increase in the sulphuric acid concentration enhances the driving force of mass transfer and chemical reactions or, to be more precise, the particle diffusion rate and the rates of reactions (a) and (b). However, if the sulphuric acid concentration is above optimal, a dense crust of $CaSO_4 \cdot 0.5H_2O$ is formed on the particles, the diffusion of H_3PO_4 is slowed down, and the physical properties of the product are inferior (the latter is said to be "smeary"). For decomposing the apatite concentrate in a continuous process of superphosphate production, the optimal sulphuric acid concentration is 67 to 68%. Corresponding to this acid concentration is the chamber temperature of 110 °C. Increasing the temperature is possible owing to the exothermic nature of reactions (a) and (b). At any rate, to speed up the ageing, sulphuric acid is taken in excess of the theoretical amount, then neutralized with ammonia or phosphorite meal.

The slowest step—maturing of superphosphate in storage—is accelerated by cooling the product and evaporating water from it, which speeds up the crystallization of monocalcium phosphate. To this end, superphosphate is pulverized and agitated in the storage silo with the result that the interfacial area is extended and regenerated, while the mass transfer rate increases.

Single superphosphate contains a great deal of the inert component $(CaSO_4)$ and a relatively small amount of P_2O_5 (16 to 20%), which is a disadvantage. The concentrated, dead-weight-free phosphoric fertilizer, or double superphosphate, is produced by acidulation of natural phosphates with phosphoric acid (see reaction (b)). After the crushed phosphate has been mixed with phosphoric acid, the resulting crystallization of monocalcium phosphate leads to setting of the reaction mass. This process takes place in reaction

chambers and lasts one to one and a half hours, and the $Ca(H_2PO_4)_2 \cdot H_2O$ crystals are formed during maturation of the product in storage.

The decomposition of apatite by phosphoric acid can also be divided into two steps. The first step associated with the liquid phase not yet saturated with monocalcium phosphate and free of its crystals involves a relatively fast diffusion of phosphoric acid accompanied by a rapid reaction at the apatite grain surface. The second slow step follows the saturation of the solution with monocalcium phosphate and onset of its crystallization, its rate being limited by the diffusion of phosphoric acid through the solid crust of the reaction products, covering the apatite grains. The rate of the slow diffusion steps when the reagents are transferred into the reaction zone and crystallization of $Ca(H_2PO_4)_2 \cdot H_2O$ occurs can be increased by bringing the phosphoric acid concentration up to the optimal level, using its excess amount, and stirring the reaction mass. In this way, the driving force and mass transfer coefficient are enhanced, while the interfacial area is extended and regenerated. In practice, the optimal concentration of phosphoric acid is maintained at 70 to 74%, and the optimal excess amount of the acid constitutes about 5% of the stoichiometry.

This work deals with acidulation of apatite with sulphuric and phosphoric acids to produce single and double superphosphates. Its purpose is to study the superphosphate ageing or maturation rate as a function of the following process parameters: acid concentration, excess acid (S : L ratio in the pulp), and residence time of the reaction mass in the reactor. The process can be monitored using the cationitic and photometric methods of determining P_2O_5 in the products, or single and double superphosphates, and in the phosphate stock. To determine CaO in the fertilizers use is made of the chelatometric (trilonometric) method.

Experimental Setup and Procedure

1. Sulphuric Acid Decomposition of Phosphate. The starting materials for this experiment are apatite concentrate or phosphorite of a known composition and 62-70% sulphuric acid. The stoichiometric amount of sulphuric acid is calculated in accordance with the raw material composition, using the following overall reaction equation:

$$2Ca_5F(PO_4)_3 + 7H_2SO_4 = 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF$$

7 moles of H_2SO_4 (686 g) are required per 3 moles of P_2O_5 (426 g), hence, 1.61 parts by weight of H_2SO_4 monohydrate are required per part by weight of P_2O_5.

Example. Calculate the amount of 68% H_2SO_4 necessary to decompose 100 g of apatite concentrate containing 39% of P_2O_5.

Solution. Required for the purpose are

$$1.61 \cdot 39.0 = 62.8 \text{ g}$$

of the monohydrate or

$$62.8 \cdot 100/68 = 92.3 \text{ g}$$

of acid containing 68% of H_2SO_4.

The total volume of the acid to decompose 100 g of apatite is

$$92.3/1.5874 = 58.2 \text{ cm}^3,$$

where 1.5874 is the density of 68% sulphuric acid at 20°C.

The acid requirements for decomposition of the impurities present in the apatite concentrate in small amounts can be ignored. For practical purposes, sulphuric acid must be taken in an amount exceeding the stoichiometric one by 5 to 10%.

To produce superphosphate, a weighed amount of apatite concentrate (or finely divided phosphorite) is placed in a porcelain cup. Sulphuric acid is poured, in a predetermined volume, into a weighed porcelain beaker having a capacity of 0.5 to 1.0 dm³, then heated to 50-70 °C. Thereafter, the apatite concentrate is slowly, within 2 to 3 minutes, charged into the beaker with the acid, the reaction mass being continuously agitated with a porcelain rod or a mechanical stirrer.

The charging over, the reagents are stirred for another 3 to 5 minutes. Then, the beaker is put into a thermostat in which the temperature of 105 to 110 °C is maintained. It takes one to one and a half hours for the superphosphate mass to mature at this temperature, just as in a batch-type superphosphate den. 90 to 110 minutes (depending on the assignment) later the beaker is removed from the thermostat, cooled, and weighed. The resulting superphosphate is crushed in a mortar, and average samples are taken for determination of the water-soluble or available P_2O_5.

Analytical Procedure. P_2O_5 in fertilizers is determined in an aqueous extract (water-soluble form) or in an ammonium citrate solution (available form), using various methods of which the standard one is the gravimetric method whereby P_2O_5 is determined by precipitation with a magnesian mixture containing magnesium phosphates and ammonium. This method is slow and arduous. More rapid ionite methods have been developed for determining P_2O_5, and phosphorus is determined by the photocalorimetric method.

Used as the cation exchanger, or ion-exchange resin, is the high-molecular resin "Wofatit R" which, if not available, can be replaced by sulphonated coal or high-molecular cation exchanger КУ-2.

When superphosphate is roiled in water with an H-cation exchanger (КУ-2 saturated with hydrogen ions), $Ca(H_2PO_4)_2$, H_3PO_4, and, partially, $CaSO_4$ pass into the aqueous extract. This is accompanied

by the following ion-exchange reactions:

$$2H[R] + Ca(H_2PO_4)_2 = Ca[R]_2 + 2H_3PO_4$$
$$2H[R] + CaSO_4 = Ca[R]_2 + H_2SO_4$$
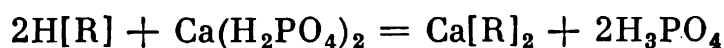
and also (as the acidity of the solution increases)

$$2H[R] + CaHPO_4 = Ca[R]_2 + H_3PO_4$$
$$3H[R] + (Fe, Al)PO_4 = (Fe, Al)[R]_3 + H_3PO_4,$$
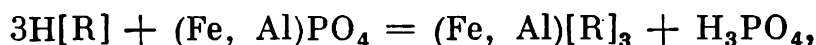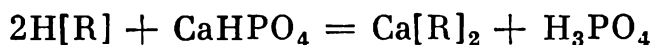
[R] being negatively charged active cation exchanger groups.

The solution resulting from exchange with the H-cation exchanger contains Ca^{2+}, SO_4^{2-}, Fe^{3+}, and Al^{3+} ions which make it difficult to continue the volumetric determination of P_2O_5. For removal of these impurities the solution is passed through a Na-cation exchanger (КУ-2 saturated with sodium ions). The associated reactions in the cationized solution are similar to those with the H-cation exchanger:

$$Na[R] + H_3PO_4 = NaH_2PO_4 + H[R]$$
$$2Na[R] + Ca(H_2PO_4)_2 = Ca[R]_2 + 2NaH_2PO_4$$
$$2Na[R] + H_2SO_4 = 2H[R] + Na_2SO_4$$
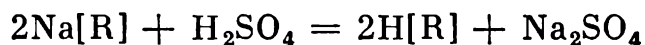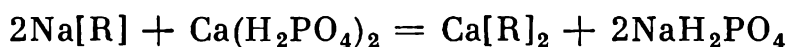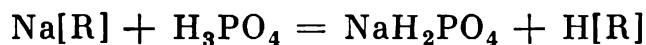
During Na-cationization, all of the phosphoric acid and other phosphorus compounds change to monosodium phosphate; P_2O_5 in solution is determined after the cationization by titration with a caustic soda solution till monosodium phosphate transforms to disodium hydrogen phosphate. The analysis requires the following chemicals prepared in advance: H- and Na-cation exchangers, bromo-cresol green (or bromo-cresol blue) and mixed indicators, as well as test substances, that is solutions having colourations corresponding to the intermediate ones in titration. For preparation of the cation exchangers, test substances, and mixed indicator see p. 34.

Prior to analysis, a weighed amount (2 to 2.5 g) of superphosphate is placed in a 500-cm³ measuring flask, 2 g of the H-cation exchanger are added into the latter together with 200 cm³ of distilled water*. The flask is stoppered and shaken for 30 minutes in a special shaker. Then, the solution level in the flask is brought to the mark by adding distilled water, the contents are stirred and strained into a dry conical flask or beaker. The H-cation exchanger mixed with the precipitate after water extraction are handed over to the laboratory assistant together with the strainer.

After that, 200 cm³ of the filtrate are transferred into a 400- to 500-cm³ beaker, 100 cm³ of water are added, and the whole is passed through a burette with the Na-cation exchanger (Fig. 8) at a rate of 60 to 80 drops per minute. The solution is collected in a 500-cm³ measuring flask into which 5 cm³ of 0.5 N HCl have been poured in

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* In this and other analyses use CO_2-free or preboiled distilled water.

advance to preset the pH of the medium. Added to the same flask is the water used to wash the Na-cation exchanger. By adding the washes the level of the solution in the flask is brought almost up to the mark, then the flask with the solution is chilled, the level is brought all the way to the mark, and the solution is stirred. This is followed by two 100-cm³ amounts of the solution being transferred from the measuring flask into conical flasks having a capacity of 250 to 300 cm³, and titration is performed. One of the portions of the solution is titrated, in the presence of 0.5 cm³ of bromo-cresol green, with 0.1 N NaOH till the solution changes its colour from yellow to light blue with an intermediate green colouration, and comparison is made with the colouration of the test substance 1. The second portion is titrated with 0.1 N NaOH in the presence of the mixed indicator (about 10 drops), till it turns pink, and its colouration is compared with that of the test substance 2.

The content of waver-soluble P_2O_5 (in % by weight) is calculated from the formula

$$C_{P_2O_5} = \frac{(v_2 - v_1)\,0.0071 \cdot 500 \cdot 500 \cdot 100m}{g200 \cdot 100} =$$

$$= \frac{(v_2 - v_1)\,8.88m}{g}, \qquad (1.32)$$

Fig. 8. Burette with cation exchanger:

1—ground-glass stopper ; *2*—granulated cation exchanger; *3*—perforated glass plate; *4*—liquid receiver

where v_1 is the amount of 0.1 N NaOH spent in the titration with bromo-cresol green, in cm³; v_2 is the amount of 0.1 N NaOH, spent in the titration with the mixed indicator, in cm³; m is a correction factor used to reduce the titre of the NaOH solution exactly to 0.1 N; g is a weighed amount of superphosphate, in g; and 0.0071 is the weight of P_2O_5, equivalent to 1 cm³ of 0.1 N NaOH, in g.

Calculation of Process Parameters from the Analysis Results. In the production of superphosphate, the product yield x is calculated as a value indicating the number of weight parts of superphosphate, obtained from one part by weight of the starting phosphate. This calculation method gives $x > 1$, unlike other processes where $x < 1$.

Under the conditions of this laboratory work, x is determined as the ratio of the weight of the produced superphosphate (G_{super}) to that of the raw phosphate (G_{phos}):

$$x = G_{super}/G_{phos}. \qquad (1.33)$$

Under actual production conditions, the yield is expressed as the ratio between the total contents of P_2O_5 in the raw material and superphosphate. The total content of P_2O_5 in the phosphate stock and phosphoric fertilizers is determined photometrically. However, if the weight of the produced superphosphate and total content of P_2O_5 in the starting phosphate are known, there is no need to determine the total content of P_2O_5 in superphosphate; if it is assumed that all of the P_2O_5 passes from the raw phosphate into the product, then

$$C_{P_2O_5(super)} = \frac{C_{P_2O_5(phos)}G_{phos}}{G_{super}} = \frac{C_{P_2O_5(phos)}}{x}. \qquad (1.34)$$

The *decomposition value of the phosphate stock* is calculated as the ratio of the content of the available P_2O_5 in superphosphate to the total content of P_2O_5 in the latter, that is

$$\eta = C_{P_2O_5(avail)}/C_{P_2O_5(total)}. \qquad (1.35)$$

2. Phosphoric Acid Decomposition of Phosphate. Acidulation of natural phosphates, particularly apatite concentrate, with phosphoric acid having a P_2O_5 concentration of 53 to 54% yields double superphosphate. The required amount of the acid is calculated, on the basis of the raw material composition and phosphoric acid concentration, from the equation of reaction

$$Ca_5F(PO_4)_3 + 7H_3PO_4 = 5Ca(H_2PO_4)_2 + HF$$
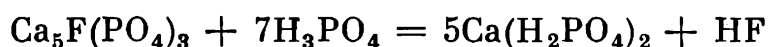
3.5 parts by weight of P_2O_5 in phosphoric acid are required per 1.5 parts by weight of P_2O_5 in the apatite concentrate, or $3.5/1.5 = 2.33$ parts by weight of P_2O_5 in phosphoric acid are required per part of P_2O_5 in the apatite concentrate. Hence, the required amount A of phosphoric acid to decompose g parts by weight of the apatite concentrate can be determined from the formula

$$A = \frac{2.33 \cdot C_{P_2O_5(apat)}g}{C_{P_2O_5(acid)}}, \qquad (1.36)$$

where $C_{P_2O_5(apat)}$ is the content of P_2O_5 in the apatite concentrate, in %; $C_{P_2O_5(acid)}$ is the content of P_2O_5 in phosphoric acid. in %; and g is a weighed amount of the apatite concentrate, in g.

Practically, phosphoric acid is taken in a 1-10%-excess amount (depending on the assignment). The calculation does not take into account the small amount of phosphoric acid expended in the reaction with the impurities present in the apatite concentrate (CaO, R_2O_3, MgO, etc.). To produce double superphosphate, a calculated and weighed amount of phosphoric acid of a given concentration (within 50 to 54% of P_2O_5, depending on the assignment) is charged into a porcelain beaker having a capacity of 0.5 dm³. The acid in the beaker is heated on a water bath up to 50°C, and while it is being

vigorously stirred by a glass rod (or mechanical stirrer), a weighed amount (25 to 50 g, depending on the assignment) of apatite concentrate is added. The apatite is poured slowly, in a narrow stream, for 1.5 to 2 minutes, then the stirring continues for another 3 to 5 minutes at 60 to 70°C (the beaker stands in the water bath). Then, the beaker with the reaction mass is transferred into a thermostat in which it is held for one to one and a half hours at 95°C. Meanwhile, double superphosphate matures. The maturation over, the beaker is withdrawn from the thermostat, cooled, weighed, and product samples are taken for analysis at definite time intervals (immediately after sampling, the next day, after two days), depending on the assignment. The samples are used to determine the content of water-soluble P_2O_5, and the decomposition value of phosphate is calculated from the results. The content of water-soluble P_2O_5 in double superphosphate is determined by the cation-exchanger method or trilonometrically from the contents of CaO and free H_3PO_4 in the solution.

Analytical Procedure. The determination of water-soluble P_2O_5 in double superphosphate using a cation exchanger is similar to that of P_2O_5 in single superphosphate and based on removal of calcium ions from the solution as the latter interacts with the H-cation exchanger, with subsequent determination of phosphoric acid by the volumetric method. The basic ion-exchange reaction involved in H-cationization is

$$2H[R] + Ca(H_2PO_4)_2 = Ca[R]_2 + 2H_3PO_4.$$
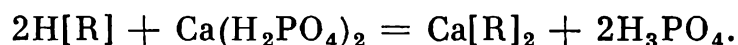
Taken for analysis is a weighed amount (1-1.5 g) of double superphosphate, which is charged into a 500-cm³ measuring flask, 300 cm³ of distilled water are added, the flask is stoppered and shaken for 30 minutes in a shaker. The solution is then strained through a paper filter, and the water used for washing the undissolved filter cake is added to make up the solution in the 500-cm³ flask to the mark. 100 cm³ of this solution are pipetted and passed through a burette with the H-cation exchanger at a rate of 2 to 4 cm³/min. The solution passed through the cation exchanger and the washes resulting from washing of the latter with distilled water are collected in a measuring flask having a capacity of 500 cm³ (the level of the solution is brought up to the mark). After careful stirring, two 100-cm³ portions of the solution are transferred from the measuring into conical flasks. The titration is carried out in the same manner as during analysis of single superphosphate, that is 5 to 7 drops of bromo-cresol green are added to the first portion and it is titrated with 0.1 N NaOH till the solution changes its colour from yellow to light blue which is then compared with the colouration of the test substance 1. Added to the second portion of the solution are 5 to 7 drops of the mixed indicator, which is followed by titration with 0.1 N NaOH till

the solution turns pink, and its colouration is compared with that of the test substance 2. The content of water-soluble P_2O_5 (in % by weight) is calculated from the formula

$$C_{P_2O_5} = \frac{m0.0071 \cdot 500 \cdot 500 \cdot 100}{100 \cdot 100} \frac{v_2 - v_1}{g} = 17.75 m \frac{v_2 - v_1}{g}, \qquad (1.37)$$

where 0.0071 is the weight of P_2O_5, equivalent to 1 cm^3 of 0.1 N NaOH, in g; m is a correction factor used to reduce the titre of the NaOH solution exactly to 0.1 N; v_1 is the amount of 0.1 N NaOH, spent in the titration with bromo-cresol green, in cm^3; v_2 is the amount of 0.1 N NaOH, spent in the titration with the mixed indicator, in cm^3; and g is a weighed amount of superphosphate, in g.

For separate determination of P_2O_5 associated with calcium ions and free phosphoric acid use is made of the trilonometric method of double superphosphate analysis, based on determination of calcium ions in the solution (aqueous extract from superphosphate) with the aid of a titrated solution of Trilon B. Trilon B is a complex compound which is essentially a sodium salt of ethylene diamine tetraacetic acid. This method is applied to determine the water-soluble form of P_2O_5 associated with calcium ions in the form of $Ca(H_2PO_4)_2$. Free phosphoric acid is determined in the same aqueous extract by titration with 0.1 N NaOH in the presence of methyl orange.

This analysis calls for an aqueous extract from double superphosphate, more concentrated than in the case of cationization. A weighed amount (2.5 g) of superphosphate is placed in a 250-cm^3 flask, 100 cm^3 of water are added, the flask is shaken for 30 minutes, the contents are strained through a paper filter into a 250-cm^3 measuring flask, and the washings (water used to rinse the conical flask containing the initial solution and to wash the filter cake) are added to bring the solution level up to the mark. The solution to be analyzed is poured into a burette and used to titrate a 0.1 N solution of Trilon B*. To this end, 4 to 5 cm^3 of the Trilon B solution are poured into a conical flask to which 70 to 80 cm^3 of distilled water are added together with 10 cm^3 of an alkaline buffer mixture** and 0.5 cm^3 of acid chrome blue, the solution then being slowly titrated with the solution under analysis and vigorously shaken after each drop has been added, till the colour changes from violet to crimson. Three

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* The Trilon B solution is prepared by dissolving 18.62 g of the reagent in 300 to 400 cm^3 of distilled water; the solution is strained into a 1-dm^3 measuring flask and its level is brought up to the mark by adding distilled water with subsequent stirring.

** The buffer mixture is prepared by dissolving 67 g ammonium chloride (c.p.) in a small amount of water, filtering the solution, mixing it with 570 cm^3 of a 25% solution of ammonia in a 1-dm^3 measuring flask, and making up the solution to the mark by adding distilled water.

samples are titrated at a time for each analysis, the first titration being approximate to roughly determine the volume of the analyzed solution, causing a change in the colouration of the indicator.

The content of CaO in the solution (in %) is calculated from the formula

$$C_{CaO} = mv0.0028 \cdot 250 \cdot 100/v_1 g, \qquad (1.38)$$

where v is the volume of 0.1 N Trilon B, taken for the analysis, in cm^2; m is a correction factor reducing the titre of the Trilon B solution to 0.1 N; v_1 is the volume of the solution to be analyzed, spent in the titration, in cm^3; g is a weighed amount of double superphosphate, in g; and 0.0028 is the amount of CaO equivalent to the content of Trilon B in 1 cm^3 of the 0.1 N solution, in g.

The results are recalculated with respect to the content of P_2O_5 (% by weight) associated with CaO in the solution, using the following formula:

$$C_{P_2O_5} = C_{CaO} 142/56, \qquad (1.39)$$

where C_{CaO} is the CaO content in the solution, in % by weight.

The content of free phosphoric acid is determined by titration of 100 cm^3 of the same aqueous extract from double superphosphate, which was used for the trilonometric determination of CaO, with 0.1 N NaOH in the presence of methyl orange. The calculation is based on the formula

$$C_{P_2O_5} = \frac{0.0071 mv250 \cdot 100}{100g} = \frac{m1.775v}{g}, \qquad (1.40)$$

where 0.0071 is the amount of P_2O_5, equivalent to 1 cm^3 of 0.1 N NaOH, in g; m is a correction factor reducing the titre of the NaOH solution to 0.1 N; v is the volume of 0.1 N NaOH, spent in the titration, in cm^3; and g is a weighed amount of double superphosphate, in g.

Preparation of the H-Cation Exchanger (Wofatit R). A burette with a perforated plate soldered at the bottom to support the cation exchanger bed (see Fig. 8) is charged with 25 to 50 g of Wofatit R. A 1% solution of HCl is passed through the burette from the top at a rate of about 1 dm^3/h, which corresponds to 8 to 10 drops per minute. The saturation continues till the concentrations of the initial and discharged acids are equalized, which is determined by titration in the presence of methyl orange. After the H-cation exchanger has been saturated with hydrogen ions, it is washed with distilled water in the same burette till methyl orange indicates a neutral reaction. The washed cation exchanger is dried for about 24 hours in air and transferred into a jar with a ground-glass stopper.

Preparation of the Na-Cation Exchanger. 25 to 50 g of Wofatit are charged into a burette through which a 4% solution of sodium chloride is passed at a rate of 8 to 10 drops per minute. The saturation continues till methyl orange indicates a neutral reaction of the discharged solution, and the Na-cation exchanger is washed with distilled water till it becomes free of the Cl$^-$ ion (test by an AgNO$_3$ solution). The Na-cation exchanger filtered using a vacuum

funnel is dried in air and transferred into a jar with a ground-glass stopper. The H- and Na-cation exchangers are easily regenerated and can be used repeatedly. The regeneration procedure is the same as that of saturation of fresh cation exchangers with hydrogen or sodium ions. H-Wofatit is regenerated by separating it from superphosphate as a result of repeated roiling with water and treated with 1% hydrochloric acid as described above.

Preparation of the Mixed Indicator. 0.6 g of phenolphthalein and 0.1 g of methyl red are dissolved in 100 cm^3 of 96% ethanol.

Preparation of the Test Substances. To prepare the test substance 1, 1 g of monosodium phosphate NaH_2PO_4 is dissolved in 250 cm^3 of distilled water. Then, 25 cm^3 of the resulting solution are diluted with 75 cm^3 of water, 7 drops of bromo-cresol green are added, and the whole is kept in a stoppered conical flask.

To prepare the test substance 2, 2.4 g of disodium hydrogen phosphate Na_2HPO_4 are dissolved in 250 cm^3 of distilled water, 25 cm^3 of the solution are diluted with 75 cm^3 of distilled water, 7 drops of the mixed indicator are added, and the prepared substance is kept in a stoppered conical flask.

Photocolorimetric Method of Determining P$_2$O$_5$. The total content of P_2O_5 in the raw phosphates and phosphoric fertilizers can be determined by means of a photocolorimeter. The *absolute photocolorimetric method* used to determine P_2O_5 in the phosphate stock and single superphosphate is based on reduction of a phosphorus-molybdenum complex with Metol in the presence of sodium bisulphite to compound $MoO_2 \cdot 4MoO_3 \cdot Me_3PO_4$ of intensely blue colour, followed by light absorption in the resulting solutions. This method has the advantage of enabling analysis in the presence of Fe^{3+}, K^+, Al^{3+}, and SiO_4^{4-} ions. It is sufficiently accurate for analysis of samples containing less than 25% of P_2O_5.

Analysis of phosphoric fertilizers containing more than 25% of P_2O_5 (double superphosphate) is based on the *differential photocolorimetric method* of determining phosphorus in the presence of a yellow phosphorus-vanadium-molybdenum complex. The measurements can be made using the ФЭК-56, ФЭК-56Н, ФЭК-57Н, and ФЭК-60 photoelectric colorimeters. This work deals with methods for measuring the optical density of solutions by means of the ФЭК-56 colorimeter.

The absolute method of determining P_2O_5 in the presence of the blue phosphorus-molybdenum complex necessitates special reagents.

Standard Potassium Dihydrogen Phosphate Solution. 1.9175 g of KH_2PO_4 are dissolved in water in a 1-dm^3 measuring flask, 10 cm^3 of sulphuric acid ($\rho = 1.84$ g/cm^3) are added, water is also added to bring the solution level up to the mark, and the contents are stirred; 1 cm^3 of this solution contains 1 mg of P_2O_5 (solution A). 50 cm^3 of the solution A are transferred into a 1-dm^3 measuring flask, made up with water to the mark, and stirred; 1 cm^3 of the solution contains 0.05 mg of P_2O_5 (solution B).

Reducing Agent Solution. 10 g of $N_2SO_3 \cdot 7H_2O$ are dissolved in 100 cm^3 of water, 2 g of Metol are added, and, after the latter has been dissolved, 600 cm^3 of a standard $Na_2S_2O_5$ solution containing

20 to 22% of SO_2 or 150 g of dry $Na_2S_2O_5$ are added; then, the contents are transferred into a 1-dm^3 measuring flask, made up with water to the mark, stirred, and strained.

Ammonium Molybdate Solution. 50 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ are dissolved in 500 cm^3 of 10 N H_2SO_4. The solution is transferred into a 1-dm^3 measuring flask, made up with water to the mark, stirred, and strained.

Sodium Acetate Solution. 600 g of $CH_3COONa \cdot 3H_2O$ are dissolved in 2 dm^3 of water and strained.

To prepare the solution to be analyzed, a weighed amount of apatite (0.3 to 0.5 g)* or phosphorite (0.5 to 0.6 g), taken from the phosphate stock, is sprinkled with water in a beaker or conical flask having a capacity of 250 to 300 cm^3, and added to the latter is a mixture consisting of 10 cm^3 of nitric acid ($\rho = 1.2$ to 1.4 g/cm^3) and 50 cm^3 of 20% hydrochloric acid ($\rho = 1.19$ g/cm^3). The mixture is first slowly heated, then boiled for 30 minutes with stirring by a glass rod. After cooling, the solution with the residue is transferred into a 250-cm^3 measuring flask and filtered ("white band" filter), the first portions of the filtrate being rejected. A definite volume V of the filtrate, containing 0.75 to 1.75 cm^3 of P_2O_5, is transferred into a 100-cm^3 measuring flask, and the solution is made up with water to 50 cm^3. For analysis of single superphosphate, sprinkle 2.0 g of the latter with water in a beaker or flask having a capacity of 250 to 300 cm^3 and add 50 cm^3 of 20% hydrochloric acid. The next steps are as described above for analysis of the phosphate stock.

Prior to photocolorimetric measurements, a calibration curve must be plotted. To this end, a series of standard solutions are prepared, containing 0.25 to 2.25 mg of P_2O_5 per 100 cm^3 of the solution, and the corresponding reagents. Dispensed into 100-cm^3 flasks with the aid of a burette are 5, 10, 15, 25, 30, 35, 40, and 45 cm^3 of the standard solution B, which corresponds to 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, and 2.25 mg of P_2O_5. 5 cm^3 of the reducing agent are added to each flask together with 10 cm^3 of the ammonium molybdate solution and allowed to stand for 10 minutes. Then, 20 cm^3 of a sodium acetate solution are added to each flask, made up with water to the mark, and stirred.

To plot the calibration curve, the optical density of each standard solution is measured with respect to water using photoelectric colorimeter with cells containing an absorbing layer 10 mm thick and a green light filter. The measurement results are used to plot the calibration curve, the abscissa representing the P_2O_5 content ($G_{P_2O_5}$), while the ordinate represents the corresponding value of optical density (D_{rel}). The calibration curve is checked daily at three points.

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* The samples are weighed to within 0.01 g.

Analysis of the sample involves the same procedure as plotting of the calibration curve, that is added to a 100-cm³ measuring flask containing a measured volume of the solution to be analyzed and 50 cm³ of water are 5 cm³ of the reducing agent and 10 cm³ of the ammonium molybdate solution, and the contents are allowed to stand for 10 minutes. Then, 20 cm³ of the sodium acetate solution are added, made up with water to the mark, and stirred. The optical density of this solution is measured photocolorimetrically under the same conditions as in the case of standard solutions (a 10-mm thick absorbing layer in the cell, green light filter), and the corresponding value of $G_{P_2O_5}$ is found from the calibration curve.

The calculation is based on the formula

$$C_{P_2O_5} = \frac{G_{P_2O_5} 250 \cdot 100}{vg1000}, \qquad (1.41)$$

where $C_{P_2O_5}$ is the P_2O_5 content in the sample, in %; $G_{P_2O_5}$ is the amount of P_2O_5, derived from the calibration curve, in mg; g is a weighed amount of the analyzed substance, in g; and v is the volume of the analyzed solution, in cm³.

Differential Method of Determining P_2O_5. This method of determining P_2O_5 in double superphosphate is based on measuring the light transmission (optical density) of a solution of a yellow phosphorus-vanadium-molybdenum complex with respect to a reference solution containing a known amount of P_2O_5. The following are the solutions required for analysis:

Ammonium metavanadate, a 0.25% solution. 2.5 g of NH_4VO_3 are charged into a 1-dm³ measuring flask, dissolved in 500 cm³ of hot water, 20 cm³ of nitric acid ($\rho = 1.4$ g/cm³) are added, the solution is made up with water to the mark and filtered.

Ammonium molybdate, a 5% solution. 25 g of $(NH_4)_6Mo_7O_{24}$ are dissolved in 500 cm³ of hot water in a 1-dm³ measuring flask, the solution is made up with water to the mark and filtered.

Reagent for Phosphates: equal volumes of solutions of nitric acid (1 : 2), ammonium metavanadate, and ammonium molybdate are mixed.

To plot the calibration curve, 1, 2, 3, 4, 5, and 6 cm³ of the standard solution A (see p. 34) are dispensed by means of a micro-burette into six 100-cm³ measuring flasks, the above amounts corresponding to 1, 2, 3, 4, 5, and 6 mg of P_2O_5. The solution in each flask is made up with water to 20 cm³, 30 cm³ of the reagent for phosphates are added, the solution is made up with water to the mark, and after 5 minutes the optical density of the solutions is measured with respect to the reference solution containing 1 mg of P_2O_5. The measurements are taken on the ФЭК-56 colorimeter at the absorbed light wavelength $\lambda = 45$ μm, in cells with an absorbing layer 10 mm thick and a light filter No. 4. The cell in the left holder

contains the reference solution, and that in the right holder contains the standard solution involved.

The iris diaphragm of the right drum is opened fully (the pointer of the right drum is set to the zero division of the optical density scale). The left compensating drum is turned to close the sector of the indicating lamp to the minimal slit. Then, the cell with the reference solution is introduced into the right light beam instead of the cell with the solution of interest. The right graduated drum is turned to close the sector of the indicating lamp, and the value of the optical density is read out from the right graduated drum. The results are used to construct the calibration curve, the P_2O_5 being plotted on the abscissa and the optical density of the solutions, on the ordinate.

The same procedure is used to determine the optical density of the double superphosphate solution under analysis (for preparation of the solution see above, p. 31), and the P_2O_5 content is determined with the aid of the calibration curve from Eq. (1.41).

LITERATURE

Methods of Analyzing Raw Phosphates, Phosphoric and Combined Fertilizers, and Phosphate Feeds, Vinnik, M. I., Yerbanova, L. N., Zaitsev, P. M. *et al.* Moscow, 1975.

Pozin, M. Ye., *The Technology of Mineral Salts*, 4th revised and expanded edition, Leningrad, 1974.

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Instructions to the Laboratory Work "Production of Phosphoric Fertilizers by Acid Decomposition of Natural Phosphates"

1. Blend the apatite concentrate with sulphuric or phosphoric acid gradually by adding portions of apatite to the acid with vigorous stirring. When producing double superphosphate, heat phosphoric acid, as it is being mixed with apatite, on a water bath. Blend the reagents under an exhaust hood and handle acids with care to avoid their contact with your hands and face.

2. Boil superphosphate in a thermostat at 105 to 110°C (single superphosphate) or 95 to 100°C (double superphosphate) for one to one and a half hours.

3. Take an average sample of the cooled product for analysis.

4. Take an aqueous extract from a weighed amount of superphosphate by adding 100 to 200 cm³ of water in a measuring flask and shaking it in a shaker for 30 minutes (add the H-cation exchanger to the weighed amount of single superphosphate). Before the shaker is switched on, make sure that the flask with the aqueous extract is firmly secured in it. When several flasks are placed in the shaker, space them widely apart.

5. Analyze the aqueous extract for the content of available P_2O_5 in superphosphate using the cation exchanger method, first by treating the extract with the H-cation exchanger, then passing it through a burette with the Na-cation exchanger. Hand over the mixture of the spent H-cation exchanger with the undissolved residue to the laboratory assistant for regeneration of the cation exchanger.

LABORATORY WORK 2. CARBONIZATION OF AMMONIACAL BRINE

Carbonization of solutions, that is their saturation with carbon dioxide, is standard chemical process used, for example, in the production of alumina by sintering techniques, in the production of soda, and so on. Carbonization of solutions results in the formation of a solid phase, such as sodium bicarbonate residue in the production of soda, aluminium hydroxide in the production of alumina, and the like. Thus, carbonization is a polyphase and multistep process involving a sequence of the following steps: diffusion of CO_2 in the gas phase, absorption of CO_2, chemical reactions and diffusion in solution, and, finally, crystallization of the product. Carbonization may serve as an example of a heterogeneous noncatalytic process occurring at low temperatures first in the G-L then G-L-S system.

All steps of soda production based on the ammonia process are essentially heterogeneous processes in the G-L or G-L-S system. Soda is produced in a closed-loop system with regeneration of the reagents (ammonia and carbon dioxide) and their return to the starting point of the process. The first step of soda production is absorption of ammonia in a strong brine of sodium salt (305 to 310 g/dm^3 of NaCl) from which the Ca^{2+} and Mg^{2+} cations have been removed in advance. Used for the absorption is regenerated ammonia from the distillation section, as well as weak gases containing NH_3 and CO_2 which are waste products at different steps of the process. The absorption of ammonia is conducted till ammoniacal brine containing 85 to 90 g/dm^3 of NH_3 is produced.

The second, main step of soda production is carbonization of the ammoniacal brine. Used for this step are carbon dioxide (85 to 90% CO_2) from sodium bicarbonate calcinators and lime-kiln gas containing 33 to 40% of CO_2. The carbonization resides in absorption of CO_2 by the ammoniacal brine, accompanied by a number of chemial reactions in the liquid phase, which lead to formation and crystallization of the solid product—sodium bicarbonate.

The general approach to intensify the absorption-desorption processes and enhance their efficiency (product yield) is through the use of advanced apparatus and intensified hydrodynamics conducive to extension and regeneration of the interfacial area and an increase in the mass transfer coefficient. According to Le Chatelier's principle, the efficiency of absorption increases with decreasing temperature and increasing pressure, while in the case of desorption, on the contrary, the yield rises with increasing temperature and decreasing pressure.

In soda production, all absorption and desorption processes are conducted in similar types of apparatus, namely, multiple-bubble-cap columns that produce a bubbling action to extend the interfacial

area between liquid and gas. These apparatus, however, are not efficient enough and, in order to ensure the necessary time of contact between liquid and gas, the bubble columns used in soda production must be multiple-staged and cumbersome.

The present work is concerned with the main step of soda production—carbonization of ammoniacal brine, which is a polyphase chemisorptive process whose overall rate is limited by the slowest steps of mass transfer from one phase to another. The absorption of CO_2 in ammoniacal brine is accompanied by chemical reactions that can be written in the following general form:

$$NaCl + NH_3 + CO_2 + H_2O \rightleftarrows NaHCO_3 + NH_4Cl \qquad (a)$$

The precipitated sodium bicarbonate is separated from the mother liquor (filter liquor) on vacuum filters and calcined in kilns at 130 °C, yielding soda ash and CO_2-containing gas:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \qquad (b)$$
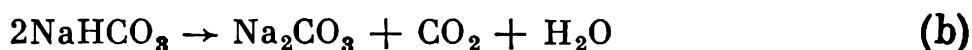
Carbonization in the production of soda ash is the main step determining the yield and quality of the product. The yield of the product—sodium bicarbonate—is determined, primarily, by the phase equilibrium in the complex system of an aqueous solution of salts $NaCl$, NH_4Cl, NH_4HCO_3, $NaHCO_3$, and precipitated $NaHCO_3$. The initial and final states of the basic process involved in carbonization can be expressed as

$$NaCl + NH_4HCO_3 \rightleftarrows NaHCO_3 + NH_4Cl \qquad (c)$$
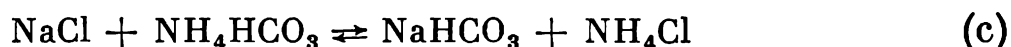
The equilibrium of reaction (c) and the equilibrium yield of precipitated $NaHCO_3$ are determined by the solubility conditions in the quaternary system $NaCl-NH_4Cl-NH_4HCO_3-NaHCO_3$ which was investigated by P. P. Fedotyev. He studied the equilibrium in this system and defined the conditions corresponding to the maximum yield of precipitated sodium bicarbonate. Since it is important, for practical purposes, to select the conditions under which a maximum yield of precipitated $NaHCO_3$ is achieved with minimum loss of the starting reagents, Fedotyev has expressed the yield of sodium bicarbonate in terms of utilization factors of the starting compounds—sodium chloride and ammonium bicarbonate (x_{Na} and x_{NH_4}). These factors can be calculated from the results of analysis of the carbonized brine:

$$x_{Na} = \frac{[Cl^-] - [Na^+]}{[Cl^-]} 100 \quad \text{and} \quad x_{NH_4} = \frac{[NH_4^+] - [HCO_3^-]}{[NH_4^+]} 100, \qquad (1.42)$$

where x_{Na} is the percentage conversion of $NaCl$ to $NaHCO_3$; x_{NH_4} is the percentage conversion of NH_4HCO_3 to $NaHCO_3$; and $[Cl^-]$, $[Na^+]$, $[NH_4^+]$, and $[HCO_3^-]$ are ion concentrations in the brine after precipitation of $NaHCO_3$, in g.eq./dm^3.

The utilization factors can be determined from the results of analyzing the brine for chlorine content, total ammonia content $[NH_{3(total)}]$, and content of free and semifixed ammonia $[NH_{3(dir)}]$, using the following formulas:

$$x_{Na} = \frac{[NH_{3(fix)}]}{[Cl^-]} 100 \quad \text{and} \quad x_{NH_4} = \frac{[NH_{3(fix)}]}{[NH_{3(total)}]} 100, \quad (1.43)$$

where $[NH_{3(fix)}]$ is the concentration of fixed ammonia present in the brine in the form of salts of strong acids NH_4Cl, $(NH_4)_2SO_4$. The maximum values of x_{Na} and x_{NH_4} correspond to carbonized brines derived from brines supersaturated with the starting reagents (397 g/dm³ of NaCl and 496 g/dm³ of NH_4HCO_3). The maximum equilibrium yield of $NaHCO_3$ (x_{Na}) is attained at 32°C and equals 84%.

The actual values of x_{Na} and x_{NH_4} are less than the theoretical ones primarily because under real conditions carbonized brines contain not more than 260 g/dm³ of NaCl and about 90 g/dm³ of NH_3. Therefore, the basic process parameter at soda plants, the utilization factor of sodium chloride (x_{Na}), varies from 65 to 75% depending on the concentration of NaCl and NH_3 in the brine, temperature, degree of saturation of the brine with ammonia and carbon dioxide, and other factors.

The amount of carbon dioxide absorbed in the brine characterizes the degree of carbonization (η) of the brine. It is defined as the ratio of the CO_2 concentration in the carbonized brine (C_{CO_2}), in g/dm³, to its total alkalinity ($C_{NH_3(total)}$), in g/dm³:

$$\eta = C_{CO_2}/C_{NH_3(total)} 100 \quad (1.44)$$

or determined from the formula

$$\eta = \frac{C_{CO_2} + 2C_{NH_3(fix)}}{C_{NH_3(total)}} 100. \quad (1.45)$$

In Eq. (1.45), the component concentrations are expressed in g-equiv/dm³, $2C_{NH_3(fix)}$ being the amount of NH_4Cl equivalent to carbon dioxide fixed in the form of $NaHCO_3$.

The actual yield of $NaHCO_3$ can be improved by increasing the concentration of NaCl in the initial brine, the degree of its ammoniation, pressure, and CO_2 content in the gas supplied to carbonization, by decreasing temperature at the end of carbonization, and other measures.

It is the purpose of this work to study the kinetics of the carbonization process and determine the effect of various process factors (reagent concentration, temperature, gas flow rate) on the yield of precipitated $NaHCO_3$ expressed in terms of the NaCl utilization factor. The carbonization rate can best be determined from variations in the composition of the carbonized brine in the course of time.

Experimental Setup and Procedure

The starting reagent to be used in this work is ammoniacal brine containing 250 to 260 g/dm^3 of NaCl and 85 to 90 g/dm^3 of NH_3. The brine is tested for the content of these components and carbonized on a setup shown schematically in Fig. 9.

The gas containing a predetermined amount of CO_2 (35 to 80%) is produced by mixing air supplied by an air blower with carbon
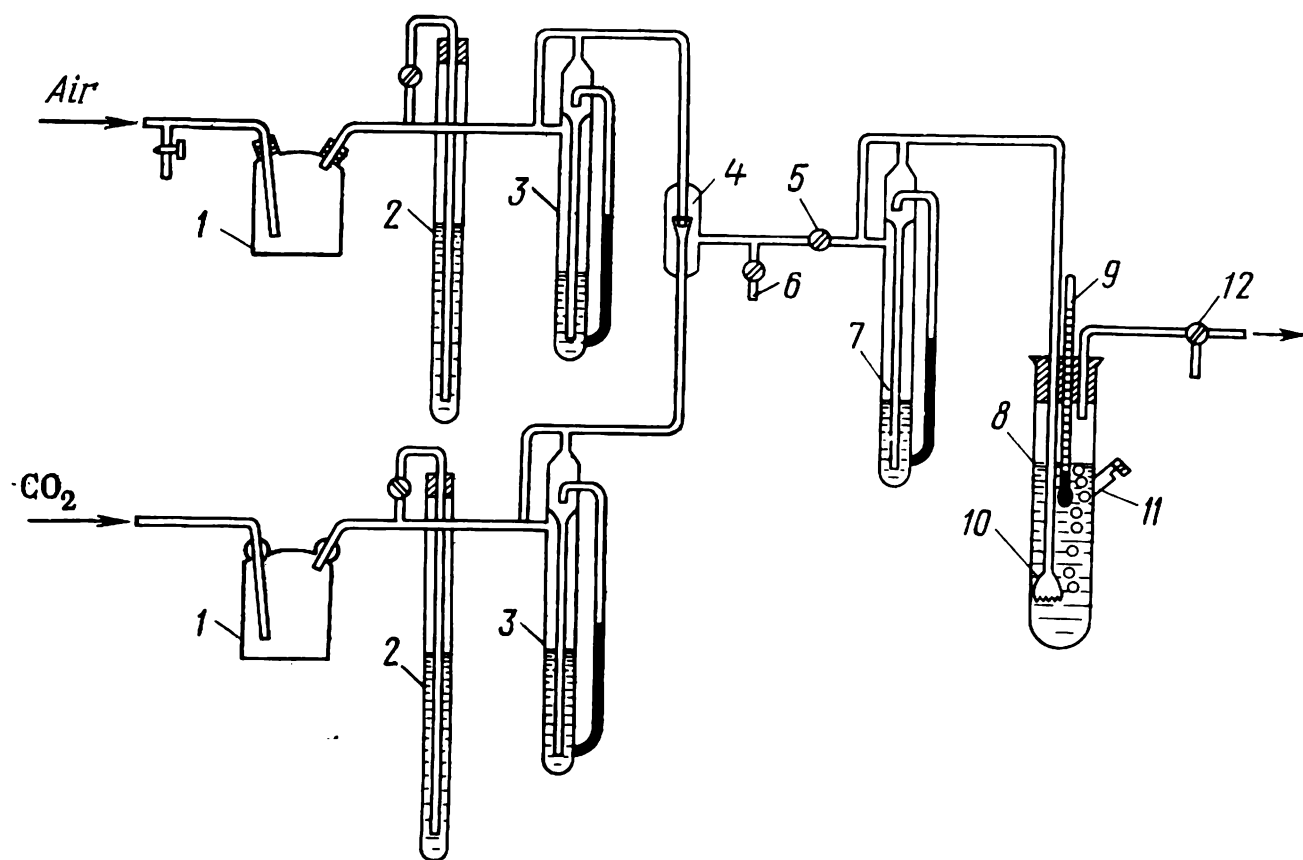
Fig. 9. Experimental setup for carbonization of ammoniacal brine:
1—surge bottles; *2*—water seals; *3, 7*—rheometers; *4*—mixer; *5*—valve; *6, 12*—three-way cock; *8*—carbonizer; *9*—thermometer; *10*—perforated cap; *11*—sampling port

dioxide from a bottle. Both gaseous components pass through surge bottles, before mixing, and rheometers for measuring the air and CO_2 flow rates. For the gas flow to be smooth and shock-free, water seals are connected to the line. The air and carbon dioxide are mixed in a mixer, and the gas mixture is sampled for analysis with the aid of a three-way cock.

The gas mixture whose composition is determined exactly by analysis is fed into a carbonizer via a rheometer measuring its flow rate. The carbonizer in the experimental setup is a glass round-bottomed cylinder 50 to 60 mm in diameter and 300 to 400 mm high. The gas is fed into the carbonizer through a perforated cap in which

the gas is bubbled. The top section of the carbonizer accommodates an outlet for tapping liquid samples for analysis. This, however, can also be done through the orifice receiving the thermometer, by periodically withdrawing the latter. The gas containing certain amounts of CO_2 and NH_3 is discharged from the carbonizer into an exhaust hood or outdoors. The outgoing gas is sampled for analysis with the aid of an outlet three-way cock.

Before the experiment, the carbonizer is charged with 250 to 300 cm^3 of ammoniacal brine of a predetermined composition (assayed by the student), which is followed by preparation of a gas mixture also of a predetermined composition. To this end, the desired air and carbon dioxide flow rates are calculated using the rheometer readings and taking into account that the total flow rate of the gas mixture must be 30 to 40 dm^3/h. The CO_2 concentration in the gas is determined exactly by means of a ГХП-1 gas analyzer with a single absorption tube filled with a KOH solution. While the gas mixture is being prepared and adjusted, the gas is released into the atmosphere through the three-way cock with the valve closed. As soon as the desired content of CO_2 in the gas has been reached, it is fed into the carbonizer after opening the cock and making sure that the system is airtight. The overall gas flow rate is preset according to the rheometer settings. Once the carbonization has been started (the gas started being fed into the carbonizer), liquid samples are taken for analysis at definite time intervals (30 to 40 minutes). Determined in the liquid are the total ammonia content as well as contents of free and semifixed ammonia and CO_2.

The carbonization is conducted for several hours, or over a predetermined period of time (3 to 4 hours), or until the composition of the liquid corresponds to that of the carbonized brine as specified by production requirements, that is the content of free and semifixed ammonia must be about 22 g/dm^3 NH_3, the total ammonia content must be in the neighbourhood of 80 g/dm^3 NH_3, and the CO_2 content must be about 77 g/dm^3. After the carbonization has been completed, the liquid is again subjected to analysis for total ammonia, CO_2, and also chlorine ions. To do this, sodium bicarbonate is filtered on a Buchner funnel with the aid of a water-jet pump, the precipitate is washed with a saturated solution of $NaHCO_3$, dehydrated with alcohol saturated with $NaHCO_3$, dried at 40 to 50°C to a constant weight, and weighed.

The analysis data are used to plot a common curve representing time variations in the contents of free and semifixed ammonia, fixed ammonia, and CO_2 in the carbonized brine and to calculate the carbonization parameters, that is utilization factors x_{NH_4} and x_{Na}, the degree of carbonization, and the yield x'_{Na} of sodium bicarbonate, expressed as percentage of the theoretically possible amount of the precipitate.

The degree of carbonization η (%) is calculated from Eq. (1.44). The yield of $NaHCO_3$ (%) is calculated using the formula

$$x'_{Na} = \frac{G_{NaHCO_3} 58.5}{G_{NaCl} 84} 100, \qquad (1.46)$$

where G_{NaHCO_3} is the amount of the dry $NaHCO_3$ residue, in g, and G_{NaCl} is the amount of NaCl in the starting brine, in g.

The value of x'_{Na} is compared with that of x_{Na}, derived from analysis of the carbonized brine. The analysis and calculation results are summarized in a table of the type proposed below:

Carbonization time, min	CO_2 content in the feed gas, %	Brine composition, g/dm³					Degree of carbonization, %	Utilization factors, %		Yield of NAHCO₃, x'_{Na}, wt. %
		total NH_3	free and se-mifixed NH_3	fixed NH_3	Cl^-	CO_2		x_{NH_4}	x_{Na}	

To complicate the task, for example, for members of a student scientific society, they should be told to determine the dependence of the carbonization rate on the CO_2 concentration in the gas or the gas flow rate. This relationship must be represented in the form of curves showing the brine composition and the degree of its carbonization versus time under various conditions (e.g. at different CO_2 concentrations in the gas). It is possible to include in the assignment determination of the effect of temperature on the carbonization process, yield of $NaHCO_3$, and the quality of sodium bicarbonate crystals. To this end, the temperature in the carbonizer must be controlled by means of a thermostat.

Analytical Procedure. The *total content of ammonium hydroxide, ammonium carbonate, and ammonium bicarbonate in the brine* ($C_{NH_3(dir)}$) is determined by titration with a strong acid in the presence of methyl orange. In this case, free and semifixed ammonia is neutralized by the acid:

$$NH_4OH + HCl = NH_4Cl + H_2O$$
$$NH_4HCO_3 + HCl = NH_4Cl + H_2O + CO_2$$

and

$$(NH_4)_2CO_3 + 2HCl = 2NH_4Cl + H_2O + CO_2$$
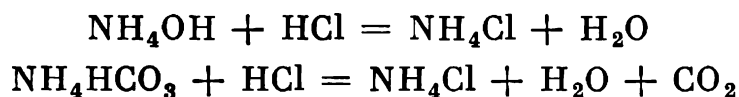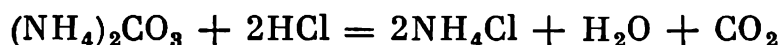
10 cm³ of brine, taken for analysis, are pipetted into a conical flask containing 40 to 50 cm³ of distilled water and 2 to 3 drops of methyl orange, and titrated with 0.1 or 1 N HCl till it changes colour from yellow to pink.

The content of free and semifixed ammonia (direct titre) is determined from the formula

$$C_{NH_3(dir)} = \frac{v0.017 \cdot 1000m}{10} , \tag{1.47}$$

where v is the amount of 1 N HCl, spent in the titration, in cm³; 0.017 is the amount of ammonia, corresponding to 1 cm³ of 1 N HCl, in g; and m is a correction factor used to reduce the titre exactly to 1 N.

The *total ammonia content* ($C_{NH_3(total)}$) is determined by back titration. The brine sample used in the previous analysis for $C_{NH_3(dir)}$ is treated with an excess amount of a strong base with the result that fixed ammonia turns free:

$$NH_4Cl + NaOH = NH_4OH + NaCl$$

$$(NH_4)_2SO_4 + 2NaOH = 2NH_4OH + Na_2SO_4$$
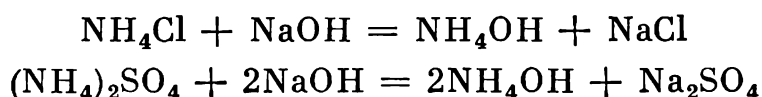
Free ammonia is driven off from the brine by boiling, whereafter the unreacted excess of the strong base is titrated with an acid.

For this analysis use is made of the neutral solution resulting from direct titration. This solution is diluted with distilled water to 100 cm³, and 50 cm³ of titrated 1 N NaOH are added. The solution is then boiled for a long period of time till the odour of ammonia disappears and, after cooling, the excess of sodium hydroxide is titrated with 1 N HCl in the presence of methyl orange.

The total ammonia content $C_{NH_3(total)}$ (g/dm³) is

$$C_{NH_3(total)} = \frac{(50-v) \, 0.017 \cdot 1000m}{10} , \tag{1.48}$$

where v is the amount of 1 N HCl, spent in the titration, in cm³.

If the sodium hydroxide and hydrochloric acid solutions do not correspond exactly to the 1 N solution, the number of cm³ of NaOH and HCl must be multiplied by respective correction factors.

The *content of fixed ammonia* $C_{NH_3(fix)}$ is determined as the difference between the total ammonia content in the brine and the content of free and semifixed ammonia, that is

$$C_{NH_3(fix)} = C_{NH_3(total)} - C_{NH_3(dir)}. \tag{1.49}$$

The *chlorine content* is determined by the argentometric method based on isolation of a poorly soluble residue of AgCl during titration of the analyzed brine with silver nitrate in an acidic medium. The end of titration is identified with the aid of an indicator forming, together with excess AgNO₃, a coloured residue.

10 cm³ of the brine to be analyzed are pipetted into a 500-cm³ measuring flask, made up with water to the mark, and stirred. 10 cm³ of the diluted brine are transferred from the measuring into a conical flask, 30 to 40 cm³ of distilled water are added, the brine

(ammonia) is neutralized using several drops of concentrated nitric acid with reference to litmus paper, and one or two drops of the acid are added to the neutral solution to create an acidic medium. Then, added into the same flask are one or two drops of a saturated K_2CrO_4 solution to be used as an indicator, which is followed by titration with $0.1\ N$ $AgNO_3$, the flask being shaken all the time, till the residue acquires a permanent brownish colouration as a result of formation of Ag_2CrO_4. The chlorine content C_{Cl} in the brine (g/dm^3) is determined using the formula

$$C_{Cl} = \frac{v0.003\ 546 \cdot 1000m}{0.2}, \qquad (1.50)$$

where v is the amount of $0.1\ N$ $AgNO_3$, spent in the titration, in cm^3, and 0.2 is the amount of the analyzate in the titrated sample, in cm^3.

The content of NaCl in the brine is determined from the formula

$$C_{NaCl} = \frac{v0.005\ 846 \cdot 1000m}{0.2}. \qquad (1.51)$$

The *carbon dioxide content in the brine* is determined by the gas-volume test whereby a weighed amount or a particular volume of the brine to be analyzed is treated with a strong acid and the amount

Fig. 10. Device for determining carbon dioxide in brine

of the liberated CO_2 is measured. The test is carried out on a setup illustrated in Fig. 10. It comprises a reaction vessel *5* with a container *6* sealed in its bottom. In the reaction vessel the sample is treated with a hydrochloric acid solution. It communicates with a measuring burette *3* having a capacity of 250 to 300 cm^3, in which the volume of the evolving carbon dioxide is measured. The compensating tube *2* and level bottle *1* are filled with an acidulated NaCl solution tinted with several drops of methyl orange.

Prior to analysis, the experimental setup is tested for air-tightness, which is done by raising the level bottle, with the three-way cock *4* closed, so that the levels of the liquid in the burette *3* and the bottle are at the same height, the volume of air in the burette is measured, and the level bottle is lowered. 5 to 10 minutes later, the air volume in the burette *3* is measured again; if it has not changed, the system is airtight. Then, the measuring burette *3* is filled to capacity with a NaCl solution with the aid of the bottle *1* and cock *4*, the latter is closed, and the bottle is put on the table. A certain amount of the brine to be analyzed (1 to 2 cm^3) is poured into the reaction vessel. 5 to 10 cm^3 of a 10% HCl solution are pipetted

into the container *6*. After that, the reaction vessel is closed tight, connected to the measuring burette through a tube with a stop cock, and turned upside down so that the acid flows out of the container and mixes with the brine sample. The resulting carbon dioxide goes into the measuring burette. As soon as the reaction is over (which can be seen from no more bubbles being formed), the reaction vessel is heated by immersing it several times into a hot water bath and allowed to cool for 30 to 40 minutes. Then, the bottle *1* is raised to equalize the liquid levels in it and in the burette and the displaced volume of CO_2 is measured. The measured volume of the evolved carbon dioxide (v) is recalculated with respect to the dry gas volume (v_0) at 0°C and $1.01 \cdot 10^5$ Pa:

$$v_0 = \frac{v273\,(P-p)}{1.01 \cdot 10^5\,(273+t)}, \qquad (1.52)$$

where P and p stand, respectively, for barometric pressure and water vapour pressure at the measured temperature, in Pa; $1.01 \cdot 10^5$ is normal pressure, in Pa; and t is temperature, in °C.

The water vapour pressure p above the saturated solution is given below.

t, °C	5	8	10	12	15	18
p, Pa	651.7	811.3	917.7	1050.7	1290.1	1556.1

t, °C	20	22	25	28	30
p, Pa	1755.6	1995	2380.7	2846.2	3192

The CO_2 content C_{CO_2} in the analyzed brine (g/dm³) is calculated from the formula

$$C_{CO_2} = 1000v_0 44/22\,410v_1, \qquad (1.53)$$

v_1 being the volume of the analyzed liquid, in cm³.

LITERATURE

Shokin, I. N. and Krasheninnikov, S. A., *The Technology of Soda*, Moscow, 1975.

Instructions to the Laboratory Work "Carbonization of Ammoniacal Brine"

1. Switch on the air blower with the three-way cock being fully open into the atmosphere, and preset the required air flow rate with the aid of the screw clamp of the cock, releasing air into the atmosphere through the cock *6* with the valve *12* closed (see Fig. 9).

2. While the gas is being bled into the atmosphere, preset the desired carbon dioxide flow rate with the aid of the rheometer, carefully and slowly opening the CO_2 bottle.

3. Analyze the feed gas composition and, if necessary, adjust it in accordance with the assignment.

4. Stop bleeding the gas into [the atmosphere and start feeding it into the carbonizer filled in advance with the initial ammoniated brine; mark the carbonization onset time.

5. Take liquid samples from the carbonizer at predetermined time intervals and analyze them.

6. When the carbonization is over, cut off the gas supply, close the bottle, and switch off the air blower. Analyze the carbonized brine, dry and weigh the precipitated sodium bicarbonate.

7. Plot a brine composition-versus-time curve using the analysis results and calculate the following process parameters: degree of carbonization, utilization factors, and bicarbonate yield based on the precipitate weight.

8. Take all the necessary precautions when handling bottles containing compressed gases. When opening the carbon dioxide bottle, first turn the main valve slightly open and control the gas flow by the pressure reducing valve.

LABORATORY WORK 3. FROTH-BED GAS ABSORPTION

General Information About Froth-Bed Processes, Design and Operating Principle of Froth Apparatus. Froth apparatus are used for heat- and mass-transfer processes with direct contact between the liquid and gas phases, such as cooling, heating, absorption, desorption, scrubbing, and drying of gases. These processes are widely applied in the chemical, coke-chemical, petroleum, gas, food, and other industries.

The froth-bed treatment of gases and liquids permits heat- and mass-transfer processes to be intensified with a relatively low power consumption. This operating mode is based on turbulization of a gas-liquid system and formation of a suspended bed of mobile unstable froth from the interacting liquid and gas. In this suspended bed, heat- and mass-transfer processes have a fast rate owing to the tremendous extension of the interfacial area, low diffusion resistance, and continuous regeneration of the interface. This is why froth apparatus operate with an intensity by far exceeding that of other reactors normally employed for processes in gas-liquid (G-L) systems, such as packed towers.

The mobile unstable froth forms on the grid of a froth apparatus with liquid and gas flowing crosswise at relatively high gas flow rates. Such a froth is produced from any liquid without frothing agents exclusively due to appropriate hydrodynamic conditions being provided in the apparatus, primarily a high gas velocity across the entire section of the latter and an upthrust to retain the froth bed on the grid.

The suspended bed of mobile froth in a G-L system is in many respects similar to a suspended (fluidized) bed in a G-S system. However, when gas flows through a liquid layer, forces interact in a more complex pattern than in a G-S system. It is assumed, in a first approximation, that five major forces interact in a G-L system, namely, those enabling suspension of the liquid, that is its detachment from the support (grid), including the force of friction

of the gas against the liquid and the hydrostatic lift, and the forces opposing suspension, that is the liquid's gravity, internal friction (viscosity), and surface tension.

When gas is let through the grid (sieve plate) supporting the flowing liquid, a gas-liquid system is formed, undergoing transformation as the gas flow rate w_g increases. First, bubbling occurs, then a froth bed is formed above the bubbling zone, which expands continuously and, ultimately, replaces the bubbling layer; at a particular gas flow rate the bubbling layer disappears, converting to
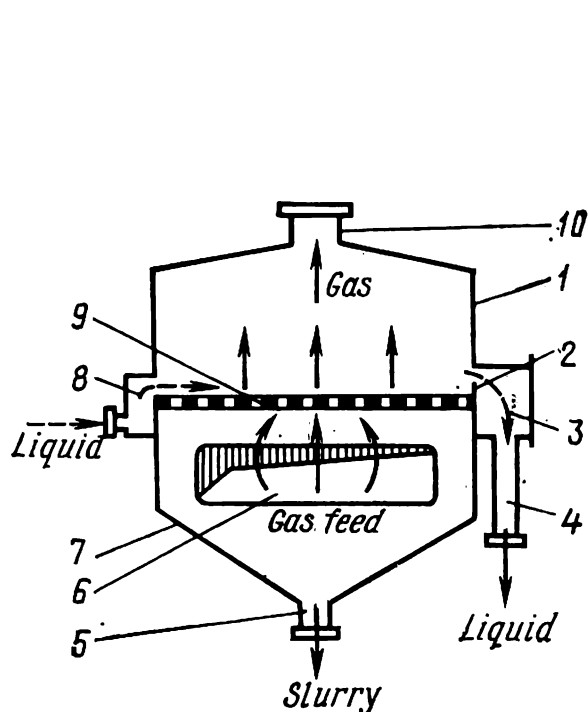
Fig. 11. Single-tray froth apparatus:

1—housing; *2*—weir; *3*—froth destruction box; *4*—discharge pipe; *5*—slurry discharge pipe; *6*—diffuser, *7*—hopper; *8*—feed box; *9*—grid; *10*—gas vent
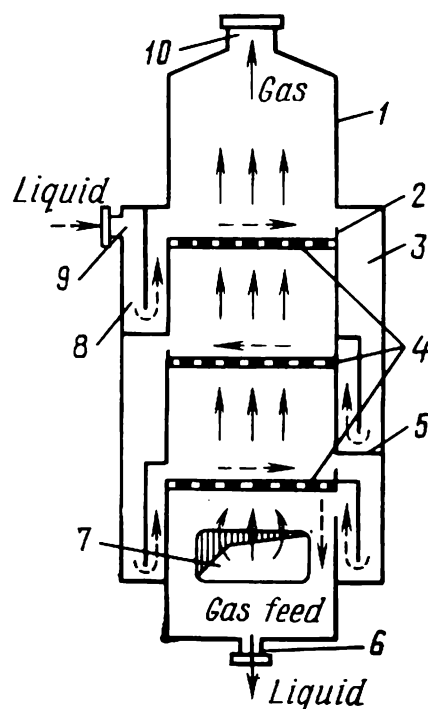
Fig. 12. Multiple-tray froth apparatus:

1—body; *2*—weir; *3*—froth destruction box; *4*—grids; *5*—water seal; *6*, *9*—pipes; *7*—diffuser; *8*—feed box; *10*—gas vent

a bed of cellular, almost static froth. The transition from bubbling to froth formation takes place at $w_g = 0.7$ to 1.3 m/s. As w_g increases further, the froth structure changes, the froth becoming mobile and turning to a heavily turbulized gas-liquid system. Such a froth is essentially a suspended liquid bed in the form of fast moving films and jets intimately interspersed with gas bubbles and jets. When frothing approaches its peak, the intensity of phase-to-phase heat and mass transfer sharply increases. As the gas flow rate continues to increase, the froth becomes more turbulent, its structure is characterized by the presence of eddies, the amount of spray above the bed increases, and at $w_g = 3$ to 3.5 m/s most of the liquid is carried away from the grid by the gas flow.

Figs. 11 and 12 show schematically single- and multiple-tray froth apparatus. The single-tray froth apparatus (Fig. 11) comprises

a hollow chamber (housing) *1* of rectangular or round cross-section with a grid which is the basis structural component of any froth apparatus. The grid is usually a perforated plate with evenly spaced holes of round, slit-like, or other shape. In some cases, grids are made of grate bars, rods, or tubes, assembled to form gaps in between. The net section of the grid is selected depending on the application and operating conditions of the apparatus and may constitute 10 to 40% of its total cross-sectional area.

The process liquid is fed onto the grid through an inlet pine and a feed box ensuring even distribution of the liquid over the grid. Gas is supplied into the space under the grid, passes through the latter, and is vented from the top part of the apparatus. Having passed through the grid openings, the gas froths the liquid on it, and the resulting froth bed, uniformly covering the entire surface of the grid, moves on the latter from the feed box toward the froth destruction box. At the point where the liquid leaves the grid, a weir is provided to ensure a certain height of the froth bed. The froth enters the froth destruction box through an overflow opening located above the weir. In the latter box, the froth is destroyed, and the liquid is discharged through a pipe.

In the multiple-tray froth apparatus (Fig. 12), the gas is supplied into the space under the bottom grid and, having passed through the openings of all of the three grids, is vented from the top portion of the apparatus. The liquid is fed onto the top grid through an inlet pipe and a feed box welded to the apparatus housing. Having flown over the top grid, the liquid enters the froth destruction box and, flowing round a partition, finds its way onto the grid second from top. In this fashion, the liquid passes sequentially over all grids and is discharged through a pipe in the bottom portion of the apparatus. The partitions in the overflow boxes create water seals preventing gas from entering the overflow area. In places where the liquid drops from the grids, weirs are welded to raise the froth on the grids. Overflow openings are arranged above them.

The basic operating parameters of froth apparatus include the froth bed height H, its hydraulic resistance ΔP_{bed}, heat transfer coefficient k_h, mass transfer coefficient k_s (if related to the froth bed surface) or k_v (if related to the bed volume), and efficiency η. The froth bed height is the most important parameter indicative of the extent of the interfacial area. In an apparatus of the above-described design, the froth bed height is proportional to that of the initial liquid bed (h_0)* and the gas flow rate w_g. The value of h_0 (mm, m) is determined by the liquid flow rate L and weir height h_w and calculated from the empirical formula

$$h_0 = \psi h_w + \varepsilon \, (3.15 - 0.005i) \, \sqrt[3]{i^2}, \qquad (1.54)$$

_____

* By the initial liquid bed height is here meant the height of the unfrothed liquid bed on the grid, before gas is passed through it.

where ψ is the coefficient of hydrostatic upthrust of the frothed liquid by the weir, ε is the coefficient of increase in h_0 due to additional resistance to the liquid flow on an operating grid, i is the liquid flow intensity per unit length or perimeter of the weir, in $m^3/m \cdot h$ ($m^3/m \cdot s$), and ($3.15-0.005i$) is the flow rate coefficient. The coefficients ψ and ε are shown in Figs. 13 and 14, with h_0 varying from 0 to 40 mm.

The froth bed height H (mm, m) can be determined experimentally or by calculations. The calculation formulas are applicable only
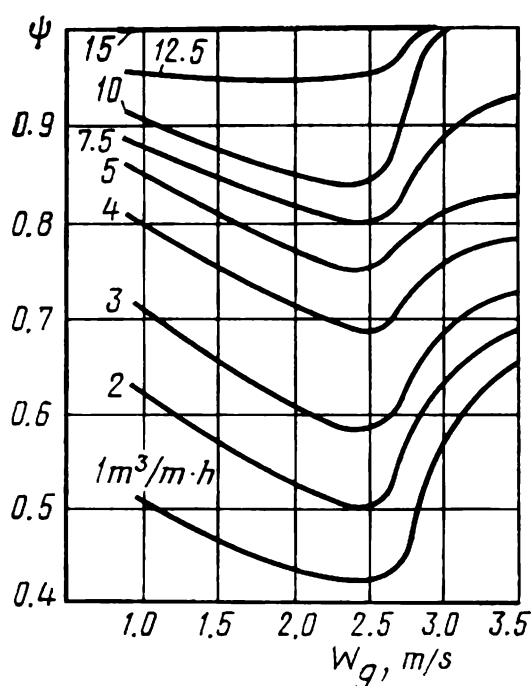
Fig. 13. Determination of coefficient ψ at different values of i
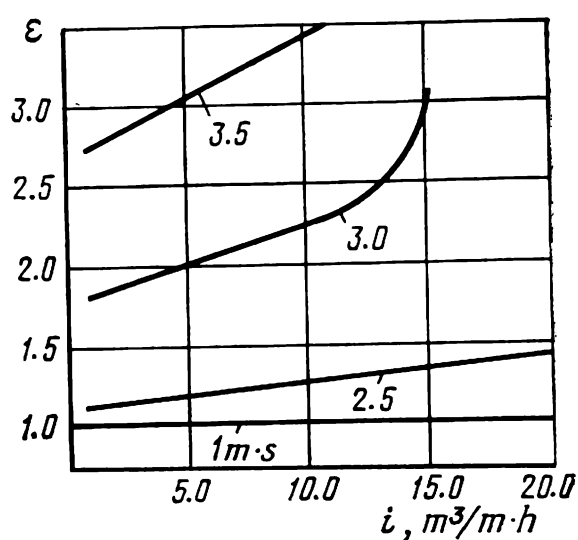
Fig. 14. Determination of coefficient ε at different values of w_g

under certain process conditions. For example, in the case of an air-water system and grids with the net cross-section S_0 ranging from 5 to 18%,

$$H = 0.35 w_g \, (h_0 + 0.075) + 2h_0, \qquad (1.55)$$

while in the case of grids with a large net cross-section ($S_0 = 18$ to 30%), when a lot of liquid leaks through,

$$H = 0.65 w_g \, (h_0 + 0.015) + 2h_0. \qquad (1.56)$$

The hydraulic resistance ΔP (Pa) of a tray in a froth apparatus is a sum of the resistance of the dry grid (ΔP_{dg}) and that of the gas-liquid bed on it (ΔP_{bed}):

$$\Delta P = \Delta P_{dg} + \Delta P_{bed}. \qquad (1.57)$$

The dependence of ΔP_{dg} and ΔP_{bed} on the basic design and operating parameters as well as physical properties of the gas and liquid

is expressed by empirical formulas, such as

$$\Delta P_{dg} = \zeta \frac{w_g^2 \rho_g}{2S_0},$$
(1.58)

$$\Delta P_{bed} = 0.85 g h_0 \rho_1 + 0.2 \sigma 10^5$$

where ζ is the coefficient of local resistance in Pa·m; g is the free fall acceleration, in m/s²; ρ_g and ρ_1 stand for the gas and liquid densities, respectively, in kg/m³; and σ is the surface tension, N/m. The basic operating parameters of a froth apparatus vary with the gas velocity (Fig. 15). The height of the froth bed increases at first, reaches a peak (at $w_g = 0.5$ to 0.7 m/s), then subsides as a result
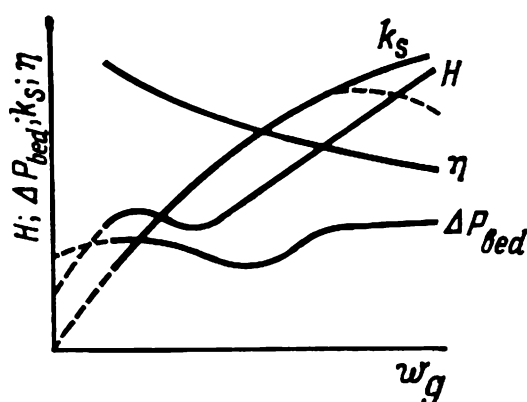
Fig. 15. Operating parameters of a froth apparatus tray versus linear gas velocity

of changes in the froth structure, reaching a minimum (at $w_g = 1$ to 1.12 m/s), and increases again due to the increased gas content. φ_g (m³/m) in the bed. The intensity of mass and heat transfer (k_s in Fig. 15) grows continuously, surpassing H, since the transition to mobile unstable froth is accompanied not only by extension of the interfacial area but also a sharp decrease in the diffusion resistances as a consequence of regeneration of the interface.

The effect of the gas velocity on efficiency is less pronounced; a slight decrease in η with increasing w_g occurs as a result of a shorter time of contact between the interacting phases (τ). ΔP_{bed} is practically independent of w_g but the total resistance ΔP of a tray increases with ΔP_{dg}.

The ratio between the amount of the liquid (L) and gas (G) flowing through the froth apparatus may vary widely. Depending on the apparatus design, grid parameters, and process conditions, the ratio between the volumes of the gas and liquid (G : L) may range from 50 to infinity. Should it become necessary to process a given volume of liquid by a less than 50-fold volume of gas, it is impossible to create a froth bed. All performance characteristics of a froth apparatus depend on the gas velocity w_g across the entire apparatus.

Description of the Absorption Plant

The laboratory absorption plant (Fig. 16) can be used to study the hydrodynamics of a froth apparatus and investigate the absorption of gas by a liquid, particularly, absorption of sulphur dioxide by a soda solution.

The laboratory model of a froth apparatus comprises a split column with a grid in the form of a round perforated steel plate
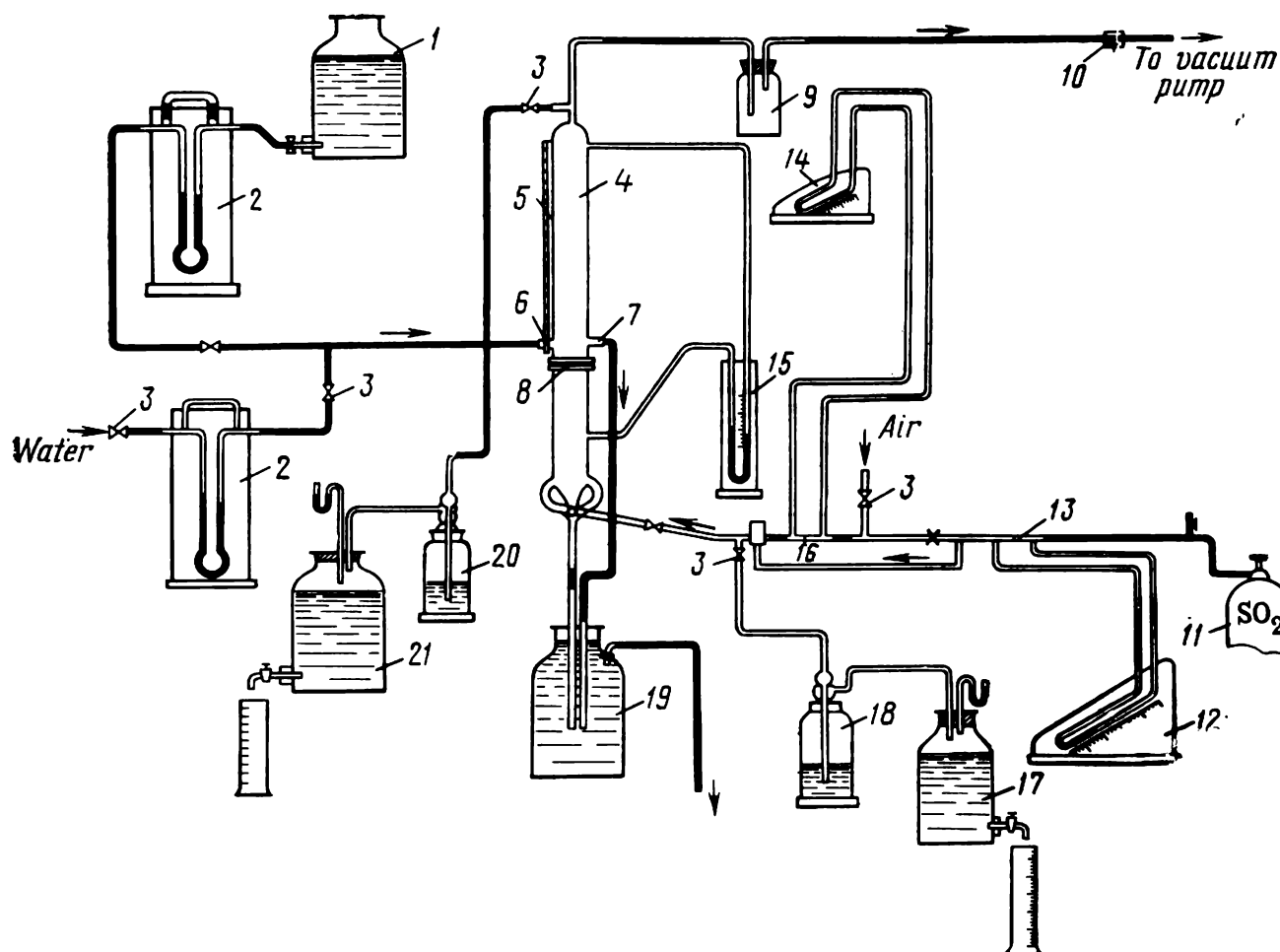
Fig. 16. Laboratory absorption plant with a froth apparatus:

1—overhead bottle; *2*—rheometer; *3*—valve; *4*—column; *5*—scale; *6*—feed pipe; *7*—discharge pipe; *8*—grid; *9*—surge bottle; *10*—screw valve; *11*—SO₂ bottle; *12, 14, 15*—differential pressure gauge; *13, 16*—orifice plate; *17, 21*—aspirator; *18, 20*—absorption vessel; *19*—liquid collector

being secured in its flanges. The grid hole diameter is 2 mm, and the spacing between the centres of holes in two different grids varies from 4 to 6 mm; depending on this spacing, the net cross-section of the grid varies from 22.66 to 10% of the total cross-sectional area of the column. The column itself is 5 cm in diameter. Its cross-sectional area equal to the area of the perforated part of the grid is 19.6 cm².

In this model, serving as the weir maintaining the required height of the liquid on the grid is the column wall from the grid up to the

overflow opening, that is the weir height is invariable for this model. Air is supplied into the space under the grid through a pipe; it froths the liquid delivered onto the grid and comes out of the upper part of the column, passing through a spray trap. The air is driven through the system by a vacuum pump installed near the exit from the latter. Water is fed onto the grid through a pipe. Its flow rate is measured by a rheometer and controlled by valves. The froth leaves the grid through an opening whose area is invariable in this model; depending on the experimentation program, this area may vary from 4 to 16 cm^2.

In an experiment involving absorption of SO$_2$ by a soda solution, the latter (15% Na$_2$CO$_3$) is applied on the grid from an overhead bottle via the rheometer into the same feed pipe, with the valves being positioned to cut off the water supply. The frothed liquid is discharged from the apparatus through the discharge pipe into a collector, and samples are taken from the collector for absorption analysis.

Sulphur dioxide enters the system from a bottle through an orifice plate with a differential pressure gauge. Air is sucked into the system through a special pipe, its flow rate being measured by means of an orifice plate with a differential pressure gauge. Before reaching the space under the grid of the froth apparatus, the air is mixed with SO$_2$ at specified ratios preset by rheometers and checked analytically.

Analysis of the gas mixture for SO$_2$ content is carried out up- and downstream of the apparatus; the gas is sampled for the analysis by means of three-way cocks with valves. The gas is tested for SO$_2$ content by way of titration with iodine in the presence of starch, till the iodine-starch solution becomes colourless. To this end, the gas under analysis is passed through an absorption vessel containing a certain amount of the titrated iodine solution into an aspirator. The total amount of the gas flowing through the system is controlled by a screw valve *10*. The hydraulic resistance of the grid with the froth bed is measured by a liquid differential pressure gauge.

The above-described system can be used to study the hydrodynamics of frothing and absorption processes.

1. Studying the Hydrodynamics of Froth Apparatus. This work is intended to elucidate the design and operation of the froth apparatus and permits an experimental study of the effect of various factors on the height and structure of the froth bed.

More specifically, it permits establishing: (1) the dependence of the froth bed height H and hydraulic resistance ΔP of the apparatus on the gas flow rate w_g over its entire cross-section, and (2) the dependence of the froth bed height and structure as well as the hydraulic resistance of the apparatus on the water flow intensity i.

To start the experiment, switch on the vacuum pump delivering air through the system and preset, using the rheometer (Fig. 16),

a desired air velocity by means of the screw valve, then open the valves in the water line and feed water onto the grid of the froth apparatus, presetting its flow rate by means of the rheometer and controlling it by the valves. By changing the air velocity w_g or the water flow rate L, depending on the assignment, measure the froth bed height H, bubbling layer height H_b, and the height h_0 of the initial liquid bed, using the scale 5. The height h_0 is measured after the air supply has been reduced to such an extent as to enable measurement of the unfrothed liquid bed without its flowing through the grid. In addition, every time there is a change in the operating conditions (gas velocity of water flow rate L), measure the hydraulic resistance of the apparatus and observe the froth bed structure, visually estimating the size and stability of the bubbles, the amount of spray, and so on. Calculate the heights of the initial liquid bed and the froth bed from the test results and compare the calculated and experimental values.

In calculating the height of the initial liquid bed using Eq. (1.54) for a given apparatus, the weir height must be assumed to be the distance between the grid and the lower edge of the overflow opening: for laboratory models of this type, h_w may be anywhere from 10 to 50 mm.

The flow intensity i must be calculated with reference to the overflow opening width l; for the froth apparatus model under consideration, $l = 20$ mm.

Example of Calculations. Calculate the initial liquid bed height h_0 and the froth bed height H for an air-water system with the water flow rate $L = 5$ dm^3/min and the air velocity $w_g = 1.5$ m/s. The weir height is $h_w = 35$ mm and the overflow opening height is $h_{of} = 60$ mm, that is the laboratory apparatus works with free overflow of the froth. The overflow opening width is $l = 20$ mm. The net section of the grid is $S_0 = 14.5\%$.

Solution. Under the specified conditions

$$i = \frac{L}{l} = \frac{0.5 \cdot 10^{-3} \cdot 60}{20 \cdot 10^{-3}} = 1.5 \text{ m}^3/\text{m} \cdot \text{h}$$

and

$$h_0 = \psi 35 + \varepsilon \, (3.15 - 0.005 \cdot 1.5) \sqrt[3]{i^2}.$$

The coefficients ψ and ε must be determined using the plots of Figs. 13 and 14. For our model of the froth apparatus with $h_{of} + h_w \cong 100$ mm and an invariable overflow opening height, we find from Figs. 13 and 14 that $\psi = 0.5$ and $\varepsilon = 1$. Then, according to Eq. (1.54),

$$h_0 = 0.5 \cdot 35 + (3.15 - 0.005 \cdot 1.5) \sqrt[3]{1.5^2} = 22.3 \text{ mm}.$$

At S_0 ranging from 5 to 18%, the froth bed height can be calculated from Eq. (1.55), that is

$$H = 0.35 \cdot 1.5 \, (3.15 + 0.075) + 2 \cdot 22.3 = 56.3 \cong 56 \text{ mm}.$$

The report summarizing this work must contain general information about the frothing conditions, the layout of the experimental

setup, and calculations of the operating parameters. The **experimental** and calculation data can best be tabulated as follows:

Measurement No.	Air velocity, w_g, m/s	Water flow rate, L, dm³/min	Flow intensity, i, m³/m·h	Initial liquid bed height, h_0, mm		Bubbling layer height, H_b, mm	Froth bed height, H, mm		Hydraulic resistance of apparatus, ΔP, Pa	Remarks*
				experimental	calculation		experimental	calculation		

* Included here must be observations of the froth bed structure, amount of spray, etc.

The report must also include curves, derived from the tabulated data, representing such frothing parameters as H and ΔP versus gas velocity w_g or water flow intensity i, and others.

2. Studying SO_2 Absorption by Soda Solution in Froth Apparatus. The absorption of SO_2 by a soda solution is a chemisorptive process, that is the physical dissolution of the gas in the liquid (absorption proper) is accompanied by the following chemical reaction in the liquid phase:

$$Na_2CO_3 + SO_2 = Na_2SO_3 + CO_2$$

As a result of this chemical reaction, the driving force of chemisorption increases, and the process is faster as compared to physical dissolution of SO_2 alone. Besides, the equilibrium vapour pressure above the soda solution is extremely low and can be ignored in calculations.

It is the purpose of this work to introduce students to frothing as applied to absorption processes and teach them to calculate their parameters. In performing this work, students determine the dependence of the coefficient of the rate of absorption of SO_2 by soda solution and the degree of SO_2 absorption on such operating conditions as the gas velocity w_g and water flow rate L.

To start the test (see Fig. 16), switch on the vacuum pump driving the gas through the system and preset the required air velocity with the aid of the screw valve; then, carefully open the valve on the SO_2 bottle and supply the necessary amount of gas for mixing with air, this amount being preset using the rheometer so as to obtain a gas mixture containing 0.5 to 2% of SO_2. The composition of the gas fed into the apparatus must be determined analytically. To this

end, open the three-way cock and let the gas flow through an absorption vessel *18* containing 2 cm³ of 0.1 *N* iodine, 1 to 2 cm³ of a starch solution, and 40 to 50 cm³ of water, with the aid of an aspirator, till the iodine-starch solution becomes colourless; then, measure the amount of the water that has come out of the aspirator so far.

The SO_2 content C_1 in the gas (% by volume) is calculated using the formula

$$C_1 = \frac{2.188}{[v273\,(P-p)/(273+t)\,P] + 2.188}, \qquad (1.59)$$

where v is the amount of the water that has left the aspirator, in cm³; 2.188 is the volume of SO_2, equivalent to 2 cm³ of 0.1 *N* iodine at 0°C and $1.01 \cdot 10^5$ Pa; P is the barometric pressure, in Pa; t is room temperature, °C; and p is the water vapour pressure at temperature t, in Pa.

The water in the aspirator must be at room temperature, that is $t_{H_2O} = t_{room}$. After the mixture composition has been adjusted as a result of analyses, feed a soda solution (about 15% of Na_2CO_3) into the system, preset its flow rate using the rheometer, in accordance with the assignment (it must be 200 to 300 cm³/min), then let the system run under these conditions for 2 minutes, and analyze the gas coming out of the froth apparatus for SO_2 content, also passing it through an absorption vessel with an iodine solution and an aspirator. For analysis of the outlet gas charge the absorption vessel with 1 cm³ of 0.01 *N* iodine, 1 to 2 cm³ of a starch solution, and 40 to 50 cm³ of water.

Calculate the SO_2 content C_f in the outlet gas (% by volume) using the formula

$$C_f = \frac{0.109}{[v273\,(P-p)/(273+t)\,P] + 0.109}, \qquad (1.60)$$

where 0.109 is the volume of SO_2, equivalent to 1 cm³ of 0.01 *N* iodine at 0°C and $1.01 \cdot 10^5$ Pa.

Before analyzing the outlet gas, measure the froth bed height H with the aid of the scale and the hydraulic resistance ΔP of the apparatus with the aid of the pressure gauge. After the test is over, repeat it in the same sequence under different conditions specified in the experimental procedure. Use the apparatus inlet and outlet gas analysis data to calculate the absorption rate coefficient k and degree of absorption η. Calculate the absorption rate coefficient k_s (kg/m²·h·Pa) related to the grid surface area, using the formula

$$k_s = G/S\,\Delta p, \qquad (1.61)$$

where G is the amount of absorbed SO_2, in kg/h; S is the surface area of the froth apparatus grid, in m² ($S = 0.00196$ m²); and Δp is the driving force of absorption, which we assume to equal the mean

logarithmic difference between the partial pressures of SO_2 in the gas before and after the absorption,

$$\Delta p = \frac{p_1 - p_f}{2.3 \log (p_1/p_f)}, \qquad (1.62)$$

where p_1 is the initial partial pressure of SO_2 in the gas, in Pa, and p_f is the partial pressure of SO_2 in the gas after absorption, in Pa.

The calculation of Δp is based on the assumption that the equilibrium pressure of SO_2 above the soda solution is negligibly small.

Calculate G from the formula

$$G = \frac{V (C_1 - C_f) \, 273 \, (P - p_r) \, \rho_{SO_2}}{100 \, (273 + t)}, \qquad (1.63)$$

where V is the space velocity of the gas in the apparatus, in m^3/h; C_1 is the SO_2 concentration in the inlet gas, in % by volume; C_f is the SO_2 concentration in the outlet gas, in % by volume; P is the barometric pressure, in Pa; p_r is the vacuum (rarefaction) in the froth apparatus, in Pa; and ρ_{SO_2} is the density of SO_2 at 0°C and 1.01×10^5 Pa, equal to 2.927 kg/m³.

The degree of SO_2 absorption $\eta(\%)$ per tray of the froth apparatus is calculated from the formula

$$\eta = \frac{C_1 - C_f}{C_1} \, 100. \qquad (1.64)$$

Example of Calculation of the Absorption Coefficient. Determine the coefficient k_s of absorption of SO_2 by soda solution and degree of absorption η with the linear gas velocity in the apparatus being $w_g = 1$ m/s, the initial SO_2 concentration in the gas being $C_1 = 5\%$ by volume, the final concentration being $C_f = 1\%$ by volume, the temperature being $t = 20°C$, the barometric pressure being $P = 100\,814$ Pa, and the vacuum in the apparatus being $p_r = 6650$ Pa.

Solution. To calculate the amount of absorbed SO_2 determine the gas flow rate V:

$$V = 3600 w_g S = 3600 \cdot 1 \cdot 0.00196 = 7 \ m^3/h,$$

$$G = \frac{7 \, (5 - 1) \, 273 \, (100\,814 - 6650) \, 2.927}{100 \, (273 + 20) \, 101\,080} = 0.711 \ kg/h.$$

The driving force of absorption is

$$\Delta C = \frac{0.05 - 0.01}{2.3 \, (0.05/0.01)} \, 1.01 \cdot 10^5 = 0.025 \cdot 10^5 \ Pa \ (0.0248 \ atm).$$

The absorption rate coefficient is

$$k_s = \frac{0.711}{0.025 \cdot 10^5 \cdot 0.001\,96} = 0.142 \ kg/(m^2 \cdot h \cdot Pa) \ [14\,650 \ kg/(m^2 \cdot h \cdot atm)].$$

The degree of absorption is

$$\eta = (5 - 1)/5 \cdot 100 = 80\%.$$

The analysis and calculation results must then be entered in the following table:

Measurement No.	Air velocity, w_g, m/s	Space gas velocity, V, m³/h	Liquid flow rate, L, dm³/h	Hydraulic resistance of apparatus, ΔP, Pa	Froth bed height, H, mm	SO₂ content in gas, % by volume		Test temperature, °C	Pressure, P, Pa	Amount of absorbed SO₂, kg/h	Absorption rate coefficient, k, kg/m²·h·mPa	Degree of absorption, η, %
						initial	final					

The tabulated data are then used to derive curves representing k_s versus gas velocity of liquid flow rate (according to the assignment).

The report must include information about gas absorption under frothing conditions, the layout of the experimental setup, calculation of the parameters, the above table, and graphs.

LITERATURE

Frothing and Froth Apparatus, Tarat, E. Ya, Mukhlyonov, I. P., Tubolkin, A. F., *et al.*, Leningrad, 1977.

Instructions to the Laboratory Work "Froth-Bed Gas Absorption"

1. Switch on the air blower (or vacuum pump) with the three-way cock as well as all the valves in the air line of the experimental setup being fully open.

2. Preset the required air velocity by means of the three-way cock and with reference to the rheometer.

3. Make sure that all pipes discharging water from the froth apparatus (overflow and drainage) are immersed into the water-filled vessel creating a water seal.

4. Slowly open the water tap till water flows at a desired rate according to the mercury rheometer.

5. At the same time, measure the froth bed height, hydraulic resistance of the apparatus, and other parameters of interest.

6. Plot the necessary curves using the experimental data under different conditions.

LABORATORY WORK 4. POLYCONDENSATION OF DICHLORO-ETHANE AND SODIUM TETRASULPHIDE (PRODUCTION OF POLYSULPHIDE RUBBERS OR THIOKOLS)

Rubbers belong to the high-molecular compounds capable of pronounced deformation under external loads and rapidly returning to the initial state after the load has been removed.

In the industrial synthesis of rubbers, use is made of diene hydro-carbons with conjugated double bonds, that is the double bonds alternate with a single one ($-C^1=C^2-C^3=C^4-$). The polymerization of such hydrocarbons involves activation of the extreme hydrocarbon atoms (1 and 4) and "opening" of the conjugated system $CH_2=CH-CH=CH_2 \rightarrow -CH_2-CH=CH-CH_2-$, as well as breaking of the double bonds at position 1-2 or 3-4. In this case, the chain may grow in the side branches:

$$
\begin{array}{c}
CH_2 \\
\parallel \\
CH \\
| \\
-CH_2-CH-CH_2-CH=CH-CH_2-
\end{array}
$$
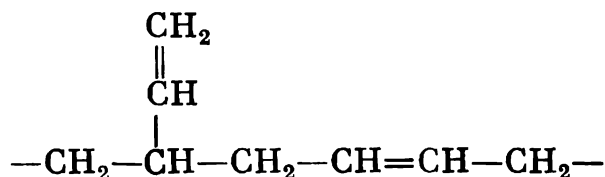
The basic monomers used in the synthesis of rubbers are buta-diene-1,3 (divinyl) and 2-methylbutadiene-1,3 (isoprene).

Depending on the application, synthetic rubbers and the cured rubbers on their basis can be divided into two groups: general-purpose rubbers going into the manufacture of tyres and many other products and special-purpose rubbers. The latter exhibit a number of specific properties. At present, the following synthetic rubbers are produced commercially: (a) general-purpose rubbers: butadiene rubber (BR), butadiene-styrene rubber (BSR), butadiene-methyl-styrene rubber (BMSR), isoprene rubber (IR), butadiene stereospecific rubber (SBR), and (b) special-purpose ones: butadiene-nitrile rubber (BNR), chloroprene rubber (Nairit), polyisobutylene, butyl rubber, thiokol and siloxane rubbers (TR). Just as all other poly-sulphide rubbers, thiokol differs sharply from natural and other synthetic rubbers, as far as its structure and formation are concerned.

High-molecular compounds are produced using two basic processes: polycondensation or polymerization of low-molecular substances. The polycondensation process is essentially a reaction of combination of the molecules of two or more different monomers, proceeding stepwise. In this reaction, the growth of the chain of the high-molecular compound involves sequential interaction of the starting substances with the growing macromolecule, accompanied by separation of a respective number of low-molecular reaction products (water, ammonia, alcohol, etc.). The ultimate composition of the resulting high-molecular compound differs from that of the initial monomers. Generally, the polycondensation process can be written as follows:

$$n(HR_1-CH_2OH) + n(HR_2-CH_2OH) \rightarrow (-R_1-CH_2-R_2-CH_2-)_n + nH_2O.$$
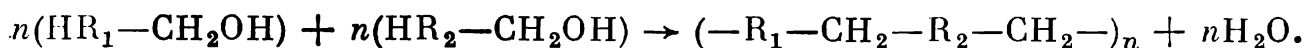
Most polycondensation reactions can be accelerated by introducing catalysts.

Thiokol rubbers are produced by noncatalytic polycondensation proceeding first in the liquid phase, then, following the formation

of a new solid phase which is the high-molecular compound (poly-condensate), in the heterogeneous L-S medium. Similarly to any reversible process, polycondensation is characterized by an equilibrium constant K and rate constants of the forward and back reactions. At equilibrium, the rate of formation of the high-molecular compound equals the rate of its degradation. If both reactions are of the second order and if it is assumed that the functional groups participate only in the polycondensation reactions without being involved in side processes, then the actual rate u_τ of the polycondensation product formation within the time interval τ is determined from the equation

$$u_\tau = u_p - u_b = k_p (1 - p_\tau)^2 - k_b p_\tau a, \qquad (1.65)$$

where u_p and u_b are the rates of polycondensation and the back reaction of degradation, respectively; k_p and k_b are the rate constants of the polycondensation and back reactions; p_τ is the number of the functional groups of the starting compound, that have entered into the polycondensation reaction within the time interval τ; and a is the amount of the low-molecular product formed within the same time interval τ. It should be remembered, though, that since the total content of the functional groups in the initial mixture is assumed to equal unity, p_τ is expressed in fractions of unity.

The constant K of reversible processes is equal to k_p/k_b. Hence, the actual rate of formation of the high-molecular compound as a result of polycondensation can be expressed as

$$u_\tau = k_p (1 - p_\tau)^2 - \frac{k_p p_\tau a}{K} = k_p \left[(1 - p_\tau)^2 - \frac{p_\tau a}{K} \right]. \qquad (1.66)$$

Thiokols or polysulphide rubbers are yielded by interaction between dihalides of the aliphatic or aliphatic-aromatic series (with halogens at the chain ends) and sodium polysulphide or other metal polysulphides:

$$n\text{Cl}-\text{R}-\text{Cl} + n\text{Na}_2\text{S}_m \rightarrow -\text{R}-\text{S}_m-\text{R}-\text{S}_m- \ldots + 2n\text{NaCl}$$
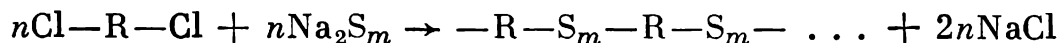
In most cases, the starting substances are dichloroethane $\text{ClCH}_2-\text{CH}_2\text{Cl}$, β,β'-dichlorodiethyl ether $\text{ClCH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{Cl}$, and β,β'-dichlorodiethyl ether of diethylene glycol

$$\text{ClCH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{Cl}$$
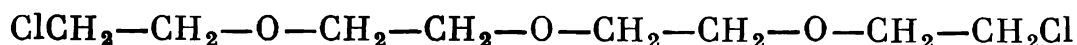
as well as sodium disulphide Na_2S, and sodium tetrasulphide Na_2S_4. If dichloroethane and sodium tetrasulphide are used as the starting compounds, the polycondensation reaction takes the form

$$n\text{ClCH}_2-\text{CH}_2\text{Cl} +$$

$$+ n\text{Na}_2\text{S}_4 \rightarrow \ldots -\text{CH}_2 \quad \text{CH}_2-\overset{\text{S}}{\underset{\text{S}}{\text{S}}}-\overset{\text{S}}{\underset{\text{S}}{\text{S}}}-\text{CH}_2-\text{CH}_2-\overset{\text{S}}{\underset{\text{S}}{\text{S}}}-\overset{\text{S}}{\underset{\text{S}}{\text{S}}}- \ldots + 2n\text{NaCl}$$
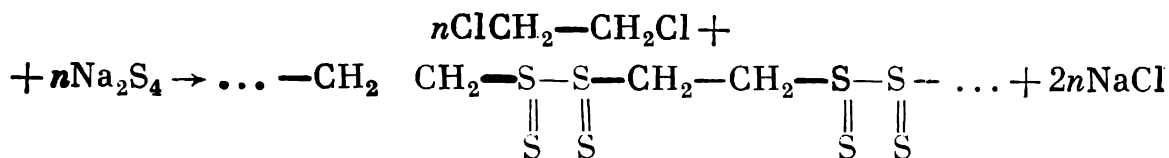
The ultimate result is polysulphide rubber containing the $(CH_2CH_2S_4)_n$ link. In view of the fact that the terminal atoms of the intermediate products are chlorine and sodium (e.g. $ClCH_2CH_2S_4 \cdot$ $\cdot CH_2CH_2S_4Na$, etc.) which readily react with each other and with the molecules of the starting substances, the polycondensation proceeds as long as it takes for high-molecular compounds to form. However, as the mass of the reacting molecules gradually increases, the polycondensation process slows down and may even stop altogether. It should be borne in mind that the main process may be accompanied by side reactions yielding mercaptan and disulphides. If a polycondensate link contains less than two carbon atoms, the resulting polycondensates are in the powder form, just as all products yielded by polycondensation with metal monosulphides. Since a great amount of heat is released during polycondensation, it is conducted as an emulsion process in an inert dispersive medium, which permits easy control of the process temperature and obtaining a homogeneous product in the form of a readily dispersable suspension which is coagulated by addition of an electrolyte (acid). The dispersers used in this process include magnesium hydroxides, hydroxides of other alkali-earth metals, and their carbonates.

The resulting polymers have a linear structure and exhibit rubber-like properties, being curable in the presence of metal oxides (usually zinc oxides). After curing, thiokol films attain high moisture and gas impermeability which is much superior as compared to that of natural or butadiene rubber vulcanizates. Thiokols are resistant to ozone, sunlight, oxygen, and various other oxidizers. The presence of a great number of polar sulphur atoms in the molecules (40 to 60%) ensures high resistance to swelling in solvents, oils, and fuels. The lower the content of polar sulphur atoms, the higher the frost resistance of thiokols. The physico-mechanical properties of thiokols and their vulcanizates are inferior to those of other synthetic rubbers. Compounders introduce large amounts of fillers (carbon black, titanium dioxide, zinc oxide, etc.) into thiokols, plus some plasticizers. The vulcanization of liquid thiokols proceeds without shrinkage.

Polysulphides have a greater density (1.6 g/cm^3) than polymers of hydrocarbons. Of all the solvents used, only carbon disulphide causes some swelling of thiokols. Weak acids and oxidizing media do not cause any perceptible degradation, as opposed to strong acids and alkaline solutions. At temperatures above 80°C, these polymers gradually degrade, and, when cooled to —15°C, thiokols lose their elasticity, becoming brittle below this temperature.

Thiokols are used in the manufacture of petrol- and oil-resistant products and components (hoses, tubing, gaskets), protective coats for the underwater parts of marine vessels, sealants, pastes for sealing tanks, ships and aircraft, adhesives, coatings, putties, paints, mould-

ing compounds, wood and leather impregnants. This work gives an insight into noncatalytic polycondensation and includes testing of thiokol for resistance to various solvents, acid and alkaline solutions.

Experimental Setup and Procedure

The experimental setup for producing thiokols comprises (Fig. 17) a round-bottomed three-necked flask *1*, a motor driving a stirrer *3*, a rheostat for controlling the stirring speed, a thermometer *6*, a dropping funnel *4*, a water bath *2*, and a reflux condenser *5*.
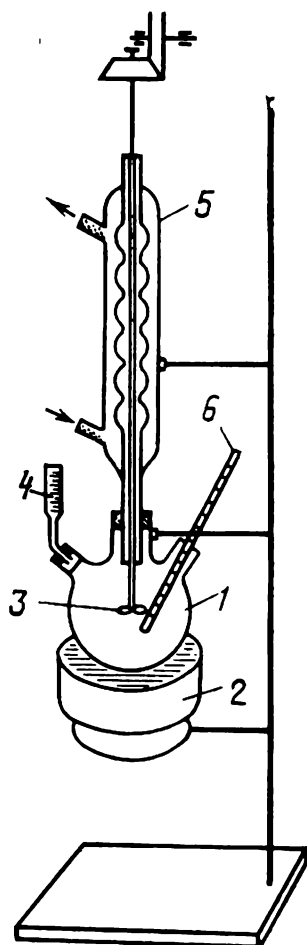
Fig. 17. Experimental setup for producing thiokol

The first step of this work is to prepare a solution of sodium tetrasulphide Na_2S_4. It is formed when sulphur is heated together with a concentrated sodium hydroxide solution, which produces the following reaction:

$$6NaOH + 10S \rightarrow 2Na_2S_4 + Na_2S_2O_3 + 3H_2O$$
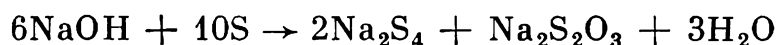
To this end, 48 to 52 cm³ of preheated water in a porcelain cup are rapidly heated to boiling, then 15.5 g of sodium hydroxide are added carefully. A calculated amount (110%) of sulphur is charged in small portions into the resulting solution, and the contents of the cup are stirred to dissolution. The reaction proceeds vigorously with an almost quantitative yield. After cooling (30 to 40°C), the clear brown solution is filtered through absorbent cotton stuffed into a short-tube funnel. The filtered solution is poured into the three-necked round-bottomed flask and heated to 70°C with the aid of the water bath. As soon as this temperature has been reached, magnesia (2% of the entire reaction mass—sodium hydroxide plus sulphur) used as the disperser is charged into the flask through one of the necks, then, while the mixture is being vigorously stirred, 10 cm³ of dichloroethane (boiling at 82 to 84°C) are added. The latter is added at a rate of 8 to 10 drops per minute at a temperature in the neighbourhood of 70°C (if necessary, cold water is added to the water bath, but at the end of the reaction it has to be reheated).

After the process is over, the contents of the flask are transferred into a clean porcelain cup, the top layer is poured out, and the residual thiokol is washed several times with warm water (40 to 50°C),

then with 20 cm³ of a 2-3% hydrochloric acid solution (till a neutral reaction as indicated by litmus paper), and again (3 to 4 times) with warm water. The thiokol is dried at 18 to 20°C, and its weight is measured to determine the yield (by drawing up a material balance). To enhance the yield of thiokol, a 10-25% alcohol solution of dichloroethane may be used.

Testing the Thiokol Properties. 0.2 g of thiokol are put, under the exhaust hood, into test tubes with 1 to 2 cm³ of solvents for observation of its stability; 15 to 20 minutes later the following entries are made in the table: $++$ — dissolution, $+$ — swelling, $--$ — no changes.

The solvents used in this test may be petrol, benzene, carbon tetrachloride, chloroform, chlorobenzene, nitrobenzene, dimethylamine, aniline, acetone, methanol, acetic acid, quinoline, 5, 10, and 20%-solutions of sulphuric and hydrochloric acids, or 5%-solution of sodium hydroxide. The results must be tabulated as follows:

Thiokol weight	Observation time	Solvents

LITERATURE

Kirpichnikov, P. A., Averko-Antonovich, A. A., and Averko-Antonovich, Yu. O., *The Chemistry and Technology of Synthetic Rubber*, Leningrad, 1975, pp. 437-445.

Reikhsfeld, V. O., Erkova, L. N., and Ruban, V. L., *Laboratory Works Involving Synthetic Rubbers*, Moscow-Leningrad, 1967, pp. 180-185.

Instructions to the Laboratory Work "Polycondensation of Dichloroethane and Sodium Tetrasulphide"

1. Check the arrangement of the experimental setup and operation of the stirrer.
2. Calculate the necessary amounts of sulphur and magnesia.
3. Pour the required amount of sodium hydroxide and the calculated amount of sulphur into boiling water.
4. Filter the resulting brown solution and decant it into the three-necked flask with a thermometer. At 70°C, introduce magnesia and add dichloroethane dropwise using the dropping funnel.
5. Carefully watch the process temperature, maintaining it at about 70°C.
6. Conduct the reaction, wash the resulting thiokol and check its resistance to various solvents and solutions only under an exhaust hood because, when processed, thiokol releases volatile substances of unpleasant odour and exciting tears.
7. Hand over the residual thiokol to the laboratory assistant.

LABORATORY WORK 5. THE KINETICS OF SULPHIDE ORE ROASTING

The roasting of sulphide ores in an air flow belongs to the typical processes employed in nonferrous metallurgy as the first step of processing nonferrous ore concentrates, in the production of sulphuric acid and cellulose, in the manufacture of sulphur dioxide, and so on. The specific features of this heterogeneous noncatalytic process can be found in the roasting of any sulphide ores, such as pyrite (FeS_2), pyrrhotite (Fe_7S_8), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), sphalerite (ZnS), and others. The overall rate of sulphide ore roasting, just as many other high-temperature roasting processes at 600°C and above, is limited by the diffusion steps of feeding the reagents (atmospheric oxygen) into the reaction zone and removal of the product (sulphur dioxide) from the latter.

The roasting of sulphide ores will be considered here using iron pyrite, which is the basic raw material (containing pyrite and impurities) in the production of sulphur dioxide, as an example. The chemical reactions involved in the roasting of iron pyrite in a fixed (filter) bed can be expressed as the following equation used in drawing up the material balance of this process:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 + Q \tag{a}$$
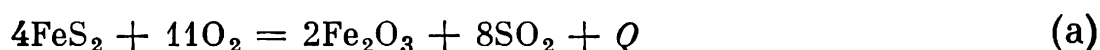
Actually, the roasting of sulphide ores involves a number of consecutive and simultaneous reactions determined, primarily, by temperature. All these reactions as well as the roasting process as a whole are irreversible. Heating in a furnace at a temperature above 500°C causes rapid dissociation of the thermodynamically unstable compound

$$2FeS_2 = 2FeS + S_2 \tag{b}$$

The released sulphur burns fast:

$$S_2 + 2O_2 = 2SO_2 \tag{c}$$

Above 600°C, the oxidation of ferrous sulphide proceeds as follows:

$$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2 + Q \tag{d}$$

in several steps with formation of FeO followed by that of Fe_3O_4 and Fe_2O_3. As a result of the catalytic action of ferric and ferrous oxides, a small amount of sulphur trioxide SO_3 is formed in the furnace after oxidation of sulphur dioxide.

The oxidation of ferrous sulphide FeS limits the overall rate of sulphide ore roasting as a consequence of the slow diffusion steps preceding the oxidation in accordance with reaction (d) and accompanying it (internal diffusion processes). During oxidation, the ferrous sulphide grains are coated with a film of ferrous oxides, hindering the diffusion of oxygen toward the unoxidized core of FeS

and the diffusion of sulphur dioxide back to the gas phase. The iron pyrite roast gas contains 7 to 15% of SO_2, 4 to 11% of O_2, up to 0.5% of SO_3, and nitrogen, their amounts varying depending on the furnace type. The oxygen to sulphur dioxide ratio in the roast gas (SO_3 is not taken into account) is calculated using the following formula:

$$C_{O_2} = n - \left[m - \frac{n(m-1)}{100} \right] C_{SO_2}, \qquad (1.67)$$

where C_{O_2} and C_{SO_2} are the oxygen and sulphur dioxide concentrations in the roast gas, in % by volume; m is the ratio of the number of the oxygen molecules entering into the reaction to that of the sulphur dioxide molecules forming as a result of the reaction (in accordance with its overall equation); and n is the oxygen content in air or some other nitrogen-oxygen mixture fed into the roasting furnace, in % by volume.

The solid residue of roasting, or pyrite cinder, consists of iron oxides (Fe_2O_3 and Fe_3O_4) and contains 0.5 to 2% of unburnt sulphur. During iron pyrite roasting, the suspended bed contains mostly Fe_3O_4 in the solid phase. In this case, the overall equation of iron pyrite combustion, used for calculation of the starting components and products, will be

$$3FeS_2 + 8O_2 = Fe_3O_4 + 6SO_2 \qquad (e)$$
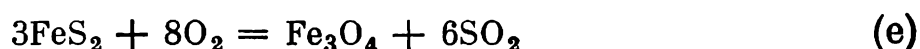
The higher roasting temperature and the greater content of SO_2 in the gas, than in the case of roasting in a fixed bed, are conducive to predominant formation of Fe_3O_4.

Optimal conditions for roasting of iron pyrite (and other raw sulphides) can be attained with the aid of the following general kinetic equation of mass transfer:

$$u = dG_{SO_2}/d\tau = k_m F \, \Delta C, \qquad (1.68)$$

where $u = dG_{SO_2}/d\tau$ is the overall roasting rate, k_m is the mass transfer coefficient, F is the interfacial area equal to the surface area of all particles, and ΔC is the driving force of roasting, dependent on the oxygen concentration in air and the sulphur content in iron pyrite.

The driving force ΔC of roasting can be enhanced by dressing sulphide ores by multiple flotation, for example, by increasing the content of pure pyrite (FeS_2) in the raw material to 90% and more, as well as by enriching air with oxygen. Practically, the oxygen concentration in the gas is increased by using an excess amount of oxygen, 1.2 to 1.8 times greater than what is required theoretically in accordance with stoichiometric equation (a) used for calculations.

The mass transfer coefficient k_m can be increased by raising temperature and intensifying the hydrodynamic conditions in the furnace in such a way as to provide for more vigorous agitation of the reagents (iron pyrite particles in the air flow). The temperature can be raised (to speed up the chemical reactions and diffusion) only to an optimal level of 800 to 1000°C, depending on the furnace type. A further increase in temperature is restricted by the thermal instability of the starting reagent, iron pyrite, which is readily caked into large aggregates with the result that the interfacial area is drastically reduced and the furnace operation is disturbed.

k_m is increased by agitation which not only minimizes the diffusion resistances but also extends and regenerates the interfacial area F between ferric sulphide and atmospheric oxygen. To this end (to decrease the internal diffusion resistances and to increase F), use is made of crushed iron pyrite with a particle size of 0.03 to 0.3 mm. The techniques of mixing the particles of the roasted material with air are determined by the furnace type and design. Three types of furnaces are normally used for roasting of sulphide ores: shelf, flash roasting, and fluidized-bed furnaces. All these furnaces operate autothermically, that is the heating in them is due to the heat generated in the sulphur and sulphide oxidation reactions.

In mechanical shelf furnaces, the crushed material is roasted in beds supported by the furnace roof arches. The roasted material is stirred (raked) and moved on the arches by mechanical stirrers. The capacity of such furnaces (type BX3) is about 225 kg of iron pyrite (45% S) per day per square meter of the furnace bottom or about 185 kg/day per cubic metre of the furnace volume.

In flash roasting furnaces, the finely divided material is pulverized in an air flow, while in fluidized-bed furnaces the roasted particles are suspended in an air flow. Fluidized-bed furnaces are characterized by maximum roasting capacity (1000 to 1800 kg/m³·day) and the highest SO_2 content in the furnace gas (up to 15% of SO_2). Flash roasting and, particularly, roasting in a fluidized bed offer the following advantages: (1) high degree of dispersion of the roasted material (which sharply reduces the internal diffusion resistances and extends the interfacial area F); (2) turbulent air flow around every particle; (3) the possibility to reduce the excess amount of air, thereby increasing the SO_2 concentration in the gas; (4) the high thermal conductivity of the fluidized bed (the heat is transferred at a high rate by convective motion of the particles) permits controlling temperature by placing coolers, or steam boiler sections, directly in the bed; (5) the mobility and fluidity of the material in the fluidized bed facilitate the removal of cinder from the furnace.

The entire process of roasting in fluidized-bed furnaces is easily controlled and can be fully automated. The most serious drawback of fluidized-bed furnaces is substantial dust loss, hence, high dust

content in the furnace gas (up to 300 g/m³). This calls for sophisti-
cated equipment to remove dust from the furnace gas.

This work is concerned with the effect of such process parameters
as air temperature and excess, sulphur content in iron pyrite, par-
ticle size, and the furnace type corresponding to a particular roasting
rate expressed as the change in the SO_2 concentration in the furnace
gas or in terms of the furnace capacity. Laboratory setups can be
used to model the process of iron pyrite roasting in a fixed or fluidized
bed, without making a replica of the roasting furnace.

Experimental Setup and Procedure

1. Roasting of Iron Pyrite in a Fixed Bed. The kinetics of iron
pyrite combustion in a fixed bed is studied using the experimental
setup illustrated in Fig. 18. The roasting is conducted in a horizontal
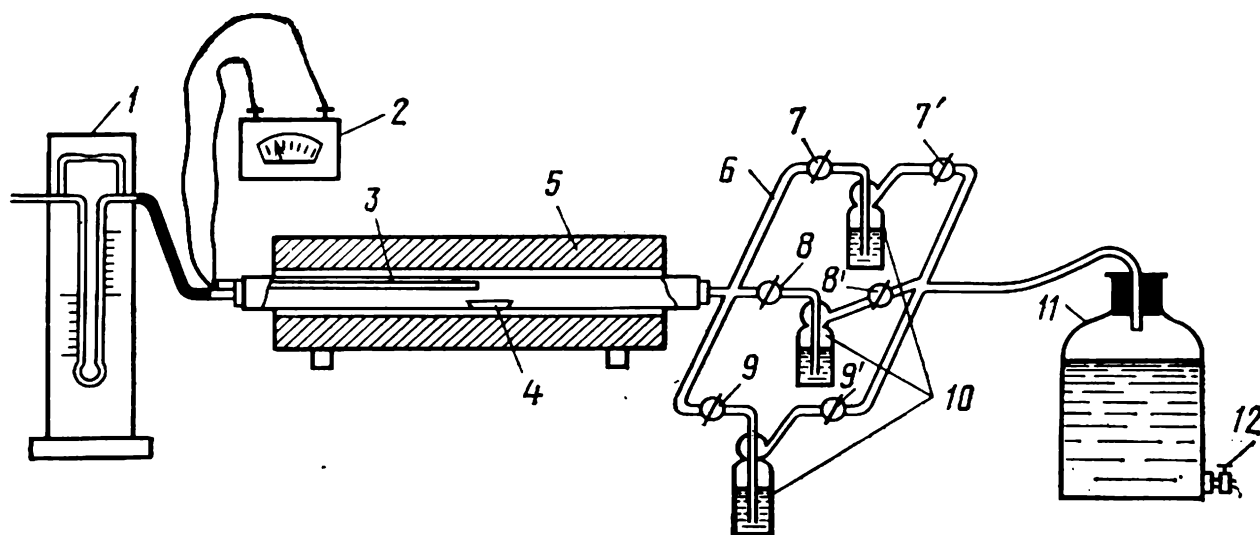
Fig. 18. Experimental setup for iron pyrite roasting in fixed bed:
1—rheometer; *2*—automatic temperature controller; *3*—thermocouple; *'4*—boat with iron
pyrite; *5*—tube furnace; *6*—glass manifold; *7-7'*, *8-8'*, *9-9'*—valves; *10*—absorption flask;
11—aspirator; *12*—aspirator valve

tube furnace with electric heating; the porcelain tube of the furnace
accommodates a boat with a weighed amount of iron pyrite. The
temperature in the furnace is measured by means of a thermocouple
and controlled automatically with the aid of an automatic tem-
perature controller of the ПСР or some other type.

The air needed to roast iron pyrite is drawn through the furnace
and the entire system by an aspirator *11*. The space velocity of the
air is measured by a rheometer *1* precalibrated at room temperature.
Upon leaving the furnace, the gas is sampled for analysis into
absorption flasks containing a measured amount of a titrated iodine
solution.

Prior to the experiment, 1 to 2 g of iron pyrite of a predetermined
composition, weighed to within 0.02 g, are charged into the boat
which is inserted, after the desired temperature has been reached,

into the furnace as close as possible to the end of the thermocouple. Then, the tube entrance is rapidly and tightly closed by a plug associated with a glass manifold. After that, the valves *7* and *7'* are opened, and air starts to be drawn through the system by means of the valve *12* of the aspirator, its flow rate being preset as soon as possible with the aid of the rheometer. The moment at which air starts passing through the absorption flasks is registered as the beginning of the experiment, using a stopwatch.

The furnace gas is analyzed continuously as it passes successively, after opening the valves *7-7'*, *8-8'*, and *9-9'*, through the absorption flasks containing a measured amount of 0.1 N iodine solution, either at definite time intervals (e.g. five minutes per flask) or till the solution becomes colourless. In the latter case, the discolouration time is measured each time. If the solution is not brought to discolouration, the furnace gas is diverted after five minutes into another absorption flask by means of the corresponding valve, the spent solution is decanted into a conical flask, and the excess iodine that has not combined with SO_2 is titrated with a 0.1 N solution of sodium thiosulphate. The emptied flasks are refilled with iodine solution, and the furnace gas analysis continues till practically all of the sulphur in the iron pyrite burns out (i.e. till the gas is free of SO_2).

The experiment is carried out in its entirety at strictly constant temperature and space air velocity. Then, the instructor changes the initial experimental conditions, that is the sulphur content in iron pyrite (within 25 to 50%), temperature (within 500 to 800°C), and the air flow rate (within 5 to 10 m³/h), and the experiment is repeated with a new weighed amount of iron pyrite.

Calculation Methods. The experimental results must be plotted in the form of kinetic curves representing the amount of burnt sulphur versus time at different temperatures or under different conditions. To do this, the amount of the sulphur burnt within the measured time intervals is calculated using the formula

$$G_S = 0.0016 \, (n v_{I_2} - m v_{Na_2S_2O_3}), \tag{1.69}$$

where G_S is the amount of sulphur burnt within a given time interval, in g; v_{I_2} is the amount of 0.1 N iodine solution in the absorption flask, in cm³; $v_{Na_2S_2O_3}$ is the amount of 0.1 N $Na_2S_2O_3$ consumed in the titration of excess iodine, in cm³; 0.0016 is the amount of sulphur (in g), corresponding to 1 cm³ of 0.1 N iodine in accordance with the equation

$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI;$$
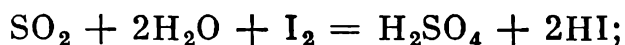
and n and m are correction factors for adjusting the normality of the solutions.

If the amount of sulphur in the weighed amount of iron pyrite of a given composition is known, the sulphur burnt within each time

interval, expressed as percentage of its total amount, that is the sulphur utilization factor, is calculated. The experimental data are also used to calculate the air excess coefficient α of air excess with respect to the theoretical amount:

$$\alpha = G_{act}/G_{theor}. \tag{1.70}$$

The theoretical amount of air G_{theor} required for complete burnout of sulphur from the weighed amount of iron pyrite of a specified composition is calculated from the stoichiometric relationships of overall reaction (a). The actual amount of air G_{act} is determined from the experimental data with known space air velocity and total duration of the experiment. The experimental and calculation results must be entered in the following table:

Test run	Weighed amount of iron pyrite, g	Sulphur content in iron pyrite, %	Sulphur content in iron pyrite, g	t, °C	Air flow rate, dm³/h	Burnout time, min	Amount of 0.1 N iodine, cm³	Amount of 0.1 N Na₂S₂O₃, cm³	Amount of burnt sulphur, %	Burnout percentage	Air excess coefficient

The tabulated data are then used to plot curves representing the amount of burnt sulphur versus roasting time under different conditions.

2. Roasting of Iron Pyrite in a Fluidized Bed. The kinetics of fluidized-bed roasting of sulphide ores can be examined on a batch or continuous experimental setup. Described in what follows are a continuous experimental setup, the experimental procedure using this setup, and calculation of process parameters from the experimental data.

The continuous experimental setup for studying iron pyrite roasting in a fluidized bed (Fig. 19) comprises a furnace in the form of an upright quartz tube housing a horizontally arranged gas-distribution grid. The furnace is heated by electric current generated in a coil. It has a heat-insulating asbestos jacket. Iron pyrite (or another sulphide ore) is continuously fed into the furnace from a bin by an auger. The cinder is continuously discharged from the furnace into a receiver associated with a collector bleeding the furnace gas into the atmosphere through a dust trap. Air is supplied into the furnace by an air blower. The air flow rate is measured by means of an orifice plate with a differential pressure gauge. The overall pressure drop in the· furnace is measured by a differential pressure gauge. The furnace

temperature is measured at three points with the aid of thermocouples connected to an electronic recording potentiometer.

The gas is sampled for analysis by means of an aspirator from the gas duct downstream of the furnace and dust trap. It is analyzed for SO_2 content iodometrically with the sample passing through an absorption flask with a titrated iodine solution. The amount of the water coming out of the aspirator corresponds to that of the unabsorbed gas.

To start the experiment, the heating (coil) of the furnace is switched on. Then, the air flow rate is adjusted with the aid of the valve on the discharge pipe of the air blower and the calibrated differential
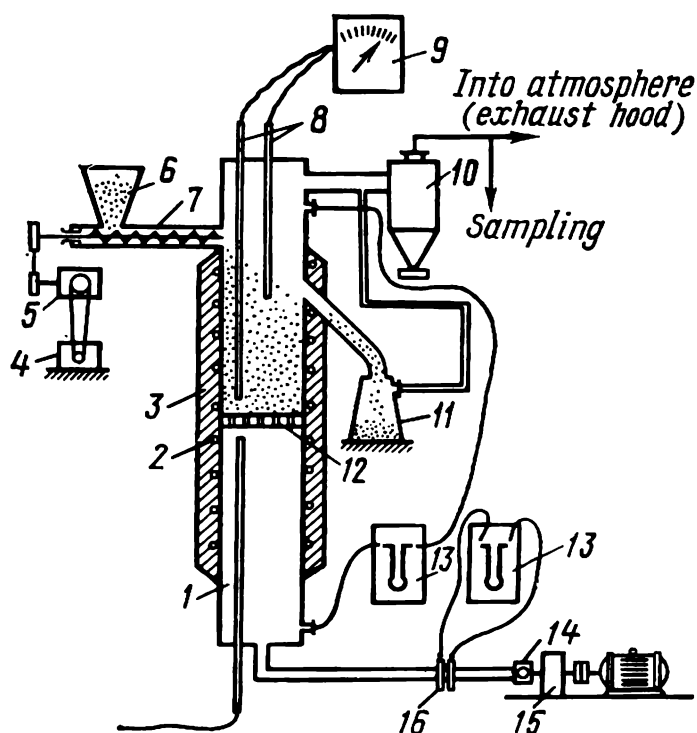
Fig. 19. Continuous experimental setup for iron pyrite roasting in a fluidized bed:

1—quartz tube; *2*—coil; *3*—asbestos jacket; *4*—electric motor; *5*—pressure regulator; *6*—bin; *7*—feed auger; *8*—thermocouples; *9*—electronic potentiometer; *10*—dust trap; *11*—cinder receiver; *12*—grid; *13*—differential pressure gauge; *14*—valve; *15*—air blower; *16*—orifice plate

pressure gauge of the orifice plate (in accordance with the assignment). As soon as the furnace temperature reaches the prescribed level, the feed auger is actuated, its rpm being preset by means of a temperature controller. From this moment on, the furnace is in operation. After a certain period of time, when the appropriate hydrodynamic conditions are attained in the furnace, the moment at which the experiment begins is registered and the gas starts being sampled for analysis (to determine the SO_2 content) according to the schedule specified in the assignment. When the experiment is over, the elapsed time is registered, a new set of conditions (temperature, air flow rate, etc.) is initiated, and the experiment is repeated.

After the experiment, the heating of the furnace is switched off, the feed auger is de-energized, the furnace is cooled by blowing air into it, and the cinder is removed from the receiver.

Calculation Methods. The results of each run under different conditions are used to determine the furnace capacity which is calculated from the material balance of roasting (based on the gas phase). Comparison of the furnace capacity at different temperatures, air flow rates, and iron pyrite particle sizes gives the optimal roasting conditions. Calculated in the first place is the critical air velocity from which the air flow rate under operating conditions is determined*. The critical rate of fluidization implies the gas (air) velocity at which the particles of the solid material become suspended.

The true fluidization rate, that is the gas (air) velocity between suspended particles (w_{tf}), can be calculated from the Mukhlyonov-Traber-Rumyantseva formula which takes the following form for laminar flow, that is at $Re \leqslant 17$ and $Ar \leqslant 1.7 \cdot 10^4$:

$$Re_t = 1.1 \cdot 10^{-2} Ar \qquad (1.171)$$

or, if the calculation is with respect to the fluidization rate (m/s),

$$w_{tf} = 10^{-2} (\rho_s d / \rho_g \nu), \qquad (1.72)$$

where $Re_t = w_{tf} d / \nu$ is the Reynolds number; $Ar = g d^3 \rho_s / \nu^2 \rho_g$ is the Archimedes number; d is the average particle size, in m; ρ_g and ρ_s are the densities of the gas and solid particles, in kg/m^3; ν is the kinematic viscosity, in m^2/s; and g is the free fall acceleration equal to 9.81 m/s^2.

The average size of the solid material particles can be determined by mesh analysis. In this case, d is calculated as the arithmetic mean between the diameter of the mesh through which pass particles of a particular size (d_1) and that of the mesh retaining the same particles (d_2): $d = 0.5 (d_1 + d_2)$. For flotation pyrite it is assumed that $d = 7 \cdot 10^{-5}$ m (or 0.07 mm). Particles of this size are suspended at laminar flow, hence, w_{tf} can be calculated from Eqs. (1.71) and (1.72). The other quantities necessary for calculation of w_{tf} at atmospheric pressure and different roasting temperatures are tabulated below.

The hypothetical rate of fluidization, that is the air velocity at the beginning of particle suspension, calculated with respect to the entire cross-section of the furnace (w_s), is determined from the formula

$$w_s = w_{tf} \varepsilon_0, \qquad (1.73)$$

where ε_0 is the porosity of the fixed bed, that is its particle-free volume. For iron pyrite particles ε_0 may be assumed to equal 0.4.

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* When iron pyrite is roasted in a fluidized bed, the air flow rate is determined by the hydrodynamics of suspension rather than the kinetics of combustion since the combustion rate is sufficiently high.

Parametre	Temperature, °C				
	0	500	600	800	1000
Air density ρ_g, kg/m³	1.252	0.45	0.40	0.325	0.268
Apparent density of pyrite ρ_s, kg/m³ (on the average)	3.6	—	—	—	—
Kinematic air viscosity ν, m²/s	$1.37 \cdot 10^{-5}$	$8.04 \cdot 10^{-5}$	$9.81 \cdot 10^{-5}$	$13.7 \cdot 10^{-5}$	$18.5 \cdot 10^{-5}$

The air velocity w during roasting must be greater than the fluidization rate w_s but less than the rate of entrainment w_e. The entrainment of particles of such a polydisperse material as iron pyrite may start at $w_e \approx 3w_s$. The air velocity at the rated furnace temperature is assumed to range from 1.5 to $2w_s$.

The air flow rate (space velocity) in m³/h, reduced to normal conditions, is given by the formula

$$V = 3600wS \ (T/T_r), \qquad (1.74)$$

where S is the tube furnace cross-section, in m²; T_r is the rated (operating) furnace temperature during the experiment, in K; and T is the temperature at which the air flow rate is measured, that is the temperature at the orifice plate (rheometer), in K.

The furnace capacity is calculated in terms of the amount of SO_2 evolved in the furnace per unit time. This calculation requires gas analysis data to determine the average content of SO_2 in the gas during the experiment. It is based on the formula

$$G_{SO_2} = VC_{SO_2}\rho_{SO_2}, \qquad (1.75)$$

where G_{SO_2} is the furnace capacity, in kg/h; C_{SO_2} is the arithmetic mean volume fraction of SO_2 in the gas during the experiment; ρ_{SO_2} is the density of SO_2, in kg/m³; $\rho_{SO_2} = 2.93 - 1.15 \cdot 10^{-2} \ t$, t being temperature, in °C.

The results of the experiments and calculations are tabulated as follows:

Test run	Test duration, min	Average particle size, d, m	Critical gas velocity, w_s, m/s	Air flow rate, V, under normal conditions, m³/h	Air flow rate, V_r, under experimental conditions, m³/h	t, °C	Gas analysis data					Furnace capacity in terms of SO_2, kg/h
							Sampling time, min	Amount of water from aspirator, cm³	Water temperature in aspirator, °C	SO_2 content in gas, % by volume	Mean SO_2 content in gas during experiment, % by volume	

The experimental results are then used to plot curves representing the furnace capacity versus such process parameters as temperature, air flow rate, and so on.

Methodological Directions. Advanced students, for example, members of student scientific societies, must calculate the material balance from the results of analysis of not only gas but also solid phase. In this case, if the sulphur content in the starting iron pyrite is known, sulphur in the cinder is determined by the rapid combustion method with subsequent titration of the absorbing solution*. The assignment may also include calculation of a fluidized-bed furnace capacity under specified conditions and comparison of the calculated value with the capacity of mechanical shelf furnaces of the BX3 type under the same conditions.

LITERATURE

Amelin, A. G., *Production of Sulphuric Acid*, Moscow, 1971.
Chemical Technology/Ed. by Mukhlyonov, I. P., Averbuch, A. Ya., Tumarkina, E. S., *et al.*, Moscow, 1977, Part II.

Instructions to the Laboratory Work "Roasting of Sulphide Ores in a Fixed Bed"

1. Calibrate the rheometer.
2. Switch on the electric heating of the furnace.
3. Charge a weighed amount of iron pyrite into the boat.
4. As soon as the furnace is heated to the desired temperature, pour a predetermined amount of 0.1 N iodine solution into the absorption flasks.
5. Place the boat with the weighed amount of iron pyrite in the middle of the furnace.
6. Rapidly adjust the required air flow rate with the aid of the aspirator valve.
7. Every 2 to 5 minutes switch over the gas flow into the next absorption flask, without waiting for discolouration of the iodine solution in the previous one.
8. After disconnection of the absorption flask, titrate the iodine solution with 0.1 N $Na_2S_2O_3$.
9. Withdraw the boat from the furnace and clean it.
10. Use crucible tongs to grip the hot boat.

Instructions to the Laboratory Work "Roasting of Sulphide Ores in a Fluidized Bed"

1. Switch on the heating coil of the furnace.
2. Preset the required air flow rate by means of the three-way cock of the air blower, with reference to the calibrated differential pressure gauge of the orifice plate.
3. As soon as the furnace is heated to the desired temperature, switch on the feed auger and adjust its rpm with the aid of a laboratory-type autotransformer.
4. When the desired hydrodynamic conditions are achieved in the furnace, start sampling gas for analysis in accordance with the schedule given in the assignment.

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* This method is described in the book *A Guide to Practical Course in the Technology of Inorganic Substances* by Pozin, M. E., Kopylev, B. A., Tumarkina, E. S., *et al.*, Leningrad, 1980.

5. After the test, reset the system of new conditions and make another run.

6. At the end of the work, switch on the furnace heating coil and auger, blow the furnace with cold air, and, after it has been cooled, discharge the cinder from the receiver.

7. Make sure that the furnace gas is vented from the furnace either into the exhaust hood or the atmosphere.

LABORATORY WORK 6. THE KINETICS OF DICALCIUM SILICATE FORMATION

Of all the binding materials used in building and civil engineering construction the most common are portland, pozzolanic, and blast-furnace cements. Portland cement is produced by crushing and grinding clinker* together with raw gypsum which is introduced in small amounts to control the cement setting time.

Blast-furnace cement is manufactured by finely grinding clinker together with granulated slag taken in an amount of 30 to 70% of the end product weight. The grinding of clinker together with acid hydraulic admixtures (tripoli, gaize, diatomite) taken in an amount of 20 to 45% gives pozzolanic cement.

The chemical composition of portland cement clinker, in terms of oxides of the basic elements, is as follows (%): CaO—64 to 67; SiO_2—21 to 25; Al_2O_3—4 to 8; Fe_2O_3—2 to 4; MgO—0.5 to 0.6; SO_3—0.3 to 0.5, and so on. Its mineral composition is rather complex. The basic constituent minerals of portland cement clinker are alite $3CaO \cdot SiO_2(C_3S)$—42 to 60%, belite $2CaO \cdot SiO_2(C_2S)$—15 to 35%, tricalcium aluminate $3CaO \cdot Al_2O_3(C_3A)$—5 to 14%, and tetracalcium aluminoferrite $4CaO \cdot Al_2O_3(C_4AF)$—10 to 16%. The total content of the above minerals is 95 to 98%. The minerals making up the cement clinker are divided into silicates $C_3S + C_2S$ and fluxes $C_3A + C_4AF$. The former two are responsible for the binding properties of portland cement. The latter two play an important role in the process of cement clinker formation, while their contribution to hardening is minor. The ratio between silicates and fluxes in portland cement clinkers varies within a relatively narrow range:

$$\frac{C_3S + C_2S}{C_3A + C_4AF} = \frac{75\text{-}82\%}{25\text{-}18\%} .$$

Thus, the manufacture of portland cement essentially boils down to obtaining a product containing the above-mentioned minerals in a particular crystalline state and ratio. The portland cement clinker formation process comprises two steps. When the starting materials are heated to about 1000°C, calcium oxide starts reacting with silica, yielding a small amount of dicalcium silicate . As the

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* Clinker is the product of burning a mixture of raw materials, containing limestone and clay taken in strictly defined proportions.

temperature is raised further to 1200 or 1250°C, the formation of dicalcium silicate (C_2S) is over, just as the formation of aluminates (C_3A) and aluminoferrites (C_4AF). Heating to a higher temperature causes most of C_2S to rapidly dissolve in the liquid phase with the result that C_2S reacts with calcium oxide in the melt, yielding tricalcium silicate (C_3S). The reaction yielding dicalcium silicate (C_2S) proceeds in accordance with the following overall equation:

$$2CaCO_3 + SiO_2 \rightarrow 2CaO \cdot SiO_2 + 2CO_2 - Q \qquad (a)$$
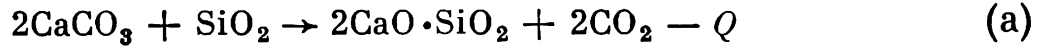
The beginning of batch burning is marked by the following lime dissociation reaction:

$$CaCO_3 \rightarrow CaO + CO_2 - Q \qquad (b)$$

The resulting calcium oxide enters into a reaction with silica to yield dicalcium silicate:

$$2CaO + SiO_2 \rightleftarrows 2CaO \cdot SiO_2 - Q \qquad (c)$$
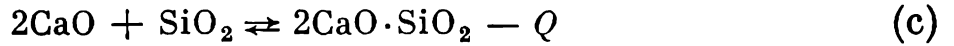
The dependence of the pressure of dissociation of lime (P) on temperature (T) can be written as

$$\log P = \frac{11\,355}{T} - 5.388 \log T + 26.238. \qquad (1.76)$$

For example, at 800°C, $P = 0.22 \cdot 10^5$ Pa, at 897°C, $P = 1.01 \cdot 10^5$ Pa and at 950°C, $P = 2.1 \cdot 10^5$ Pa. The equilibrium constant K_{eq} of the $CaCO_3$ dissociation reaction is expressed as

$$K_{eq} = p_2 p_3 / p_1, \qquad (1.77)$$

where p_1, p_2, and p_3 stand, respectively, for the $CaCO_3$, CaO, and CO_2 vapour pressures.

In the case of solids, the values of p_1 and p_2 will be practically constant within the specified temperature range (1000 to 1250°C), and the ratio $p_2/p_1 = C$ will also be constant. Hence, the expression for the equilibrium constant can be written as

$$K_{eq} = C p_3, \qquad (1.78)$$

that is the equilibrium constant is a function of only the CO_2 vapour pressure. The $CaCO_3$ dissociation rate can be expressed in the following terms:

$$u = dG/d\tau = k_2 p_2 p_3 - k_1 p_1, \qquad (1.79)$$

where $k_2 p_2 p_3$ is the dissociation rate of lime and $k_1 p_1$ is the rate of the reaction in which $CaCO_3$ is formed from CaO and CO_2.

In view of the fact that the rate of the back reaction at a maximum degree of dissociation is negligibly low, it may be assumed that

$$u = dG/d\tau = k_2 p_2 p_3, \qquad (1.80)$$

that is the lime dissociation rate varies with the CO_2 vapour pressure. The process rate increases with the burning temperature. Lime dissociates at 900 to 1000°C. At 1000°C, a small amount of dicalcium silicate is formed. At higher temperatures, its yield sharply increases. Dicalcium silicate C_2S exists in the form of α, α', β, and γ modifications. The highest-temperature modification is α-C_2S. When cooled to 1450°C, α-C_2S transforms to β-C_2S. In portland cement, C_2S is present in the β form. To produce β-C_2S, the burning step is performed twice at 1450 to 1500°C with exposure to the maximum temperature for 3 hours, followed by rapid cooling. Prior to the second burning, 0.5% of B_2O_3 are added to stabilize the β form. The end product must contain not more than 1% of free calcium oxide.

In describing the kinetics of dicalcium silicate formation, one should use the simplified Ginstling-Brounshtein equation

$$\eta = 1 - {}^2/_3 x - (1 - x)^{2/3} = k\tau, \qquad (1.81)$$

where η is the product yield, x is the percentage conversion, k is the rate constant, in min^{-1}, and τ is time, in min.

Eq. (1.81) has been derived in experiments with monodisperse systems and is based on the assumption that the particles are spherical. The introduction into Eq. (1.81) of the initial specific surface S_0 and temperature has extended the area of its application in chemical-engineering calculations at different temperatures. The empirical form of Eq. (1.81), derived by Sychev, Kichkina, and Astakhova, with dimensional coefficients is

$$\eta = 1.75 \cdot 10^{-6} (T - 1173) e^{3.22 \cdot 10^{-3} S_0} + 3.55 \cdot 10^{-6} S_0^{1.25 - 7800/\tau e^T}, \qquad (1.82)$$

T, being the absolute temperature, in K, and e being the base of natural logarithms.

This work deals with the kinetics of formation of dicalcium silicate $2CaO \cdot SiO_2$—one of the basic components of cement clinker—at different temperatures.

Experimental Setup and Procedure

All the starting raw materials used in the preparation of clinker components, or portland cement, are first finely ground (till they pass through a 4900 mesh/cm² sieve) in a laboratory-type ball mill or manually, in a mortar. The starting mix (50 to 100 g) is calculated according to the overall equation of dicalcium silicate formation. The grinding is done simultaneously with stirring over a period of time depending on the type and amount of the mix—typically 20 to 30 minutes.

The mix is sprinkled (5 to 10% of water) till a consistent paste is formed, which is then shaped into cubes, cylinders, or spheres

(about 10 mm in height and diameter). The specimens can be prepared on hydraulic presses under a pressure of 20 to 30 MPa. The prepared specimens are placed on a magnesite tray and inserted into a muffle where they undergo preliminary burning at 900 to 1000°C till dissociation of lime; exposure at this temperature lasts 30 minutes. The temperature is then raised at a rate of 150 to 250 deg/h. The specimens on the tray are then rapidly put into a high-temperature Silit kiln preheated to the desired temperature (ranging from 1200 to 1400°C) and allowed to stay at this temperature for 5, 10, or 30 minutes, according to the assignment.

Fig. 20. Silit kiln:
1—body; *2*—Silit rods; *3*—frame; *4*—bottom

The heating elements in such kilns are specially treated Silit rods. The maximum operating temperature of the kiln is 1400°C. It comprises a body (Fig. 20) secured on a frame. The Silit rods are arranged along the walls of the kiln body, with contacts being attached to their ends. The kiln bottom is lowered for loading and unloading, and during burning it remains in the hole in the lower part of the kiln body. The burnt specimens are cooled in air. To calculate the amount of the resulting dicalcium silicate, one must determine the uncombined (free) oxide.

In doing so, one must not use aqueous solutions interacting with the clinker and forming an additional amount of free calcium oxide. There are several quantitative methods of determining free CaO. The saccharate method (which is the simplest) involves treatment of a weighed amount of the finely ground material with a 10% sugar solution, followed by titration of the resulting calcium saccharate solution with 1 N HCl in the presence of the phenolphthalein indicator.

The ethyl-phenolate method is based on treatment of the sample with a mixture of anhydrous phenol and absolute alcohol; the calcium phenolate formed from free CaO is titrated in the filtrate with 1/15 N HCl. The most accurate is the ethyl-glycerate method.

Analytical Procedure. The determination of free lime in burnt specimens is based on dissolution of the uncombined lime in a hot solution of the mixture of anhydrous glycerine and absolute alcohol, yielding calcium glycerate:

$$CaO + C_3H_8O_3 \rightarrow CaC_3H_6O_3 + H_2O \qquad (d)$$
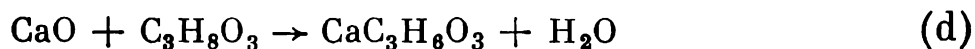
which is titrated with an alcohol solution of benzoic acid:

$$CaC_3H_6O_3 + 2C_6H_5COOH \rightarrow C_3H_8O_3 + Ca(C_6H_5COO)_2 \qquad (e)$$

1 g of a freshly ground specimen is placed in a dry conical flask having a capacity of 150 cm³ and containing 50 to 60 cm³ of a glycerine-alcohol solvent, the flask being connected to a ground reflux condenser. The mixture is vigorously shaken, boiled for 5 to 10 minutes till it turns pink, the flask is disconnected from the reflux condenser, and the hot mixture is titrated with a solution of benzoic acid in absolute alcohol till the pink colouration disappears. This procedure is repeated till the pink colouration reappears after the mixture has been heated for 15 to 20 minutes. At this point, the determination can be considered as complete. The percentage content of free calcium oxide is calculated using the formula

$$CaO_{free} = vT100/g, \qquad (1.83)$$

where v is the amount of the benzoic acid solution, spent in the titration, in cm³; g is the weighed amount of the mixture, in g; and T is the titre of the benzoic acid solution, in g CaO/cm^3 of the solution.

Fig. 21. Process rate constant versus temperature
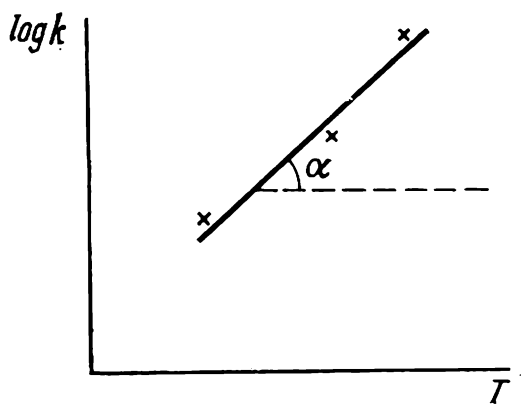
Preparation of Reagents for Analysis. Used for analysis is 100% ethyl alcohol, glycerine, benzoic acid, and absolutely dry glassware.

Glycerine-Ethyl Mixture. 15 g of dry $BaCl_2$ are added to 200 cm³ of glycerine at 100 to 125°C (for more complete dissolution of free lime during analysis and more distinct change in colouration). Chilled glycerine is mixed with 1000 cm³ of absolute alcohol and 3 cm³ of an alcohol solution of phenolphthalein.

Titrated 0.1 N Solution of Benzoic Acid. 12.25 g of C_6H_5—COOH predried over sulphuric acid are dissolved in 1 dm³ of alcohol. 30 cm³ of the glycerine-ethyl mixture and 0.04 to 0.05 g of freshly burnt CaO are charged into a dry 150-cm³ flask for titration. The flask is coupled with a reflux condenser, the mixture is heated to boiling and boiled for 10 to 15 minutes on an electric heater covered with a sheet of asbestos. After disconnecting the reflux condenser from the flask, the hot solution is titrated till it turns pink. The titre T of the benzoic acid solution is calculated using the formula

$$T = g/v,$$

where g is the weighed amount of lime, in g, and v is the amount of the benzoic acid solution, in cm³.

The percentage conversion x characterizing the amount of lime combined in calcium silicate is determined from the equation

$$x = (CaO_{total} - CaO_{free})/CaO_{total}, \qquad (1.84)$$

where CaO_{total} is the CaO content in the initial mixture, in % by weight, and CaO_{free} is the amount of CaO uncombined in dicalcium silicate, in % by weight.

Assuming that the analyzed mixture is monodisperse, the process rate constant k is calculated using the Ginstling-Brounshtein equation (1.81), and the results are tabulated as follows:

$t,$ °C	$\tau,$ min	x	$2/3\ x$	$\left(1-\frac{2}{3}x\right)$	$(1-x)$	$\log(1-x)$	$\frac{2}{3}\log(1-x)$	$(1-x)^{2/3}$	k

The tabulated data are used to plot an $x = f(\tau)$ curve for the specified temperatures. The calculated averaged values of k (for $\tau = 5$, 10, 30 min) at the specified temperatures are used to plot $\log k$ versus T (Fig. 21) with a view to graphically determining the activation energy E for this process. Its value is characterized by the slope of the straight line $(\tan \alpha)$ drawn through the experimental points toward the abscissa. The activation energy can be calculated from the Arrhenius equation

$$k = k_0 e^{-E/RT}. \tag{1.85}$$

For two known values of k at temperatures T_1 and T_2, Eq. (1.85) can be transformed to

$$E = \frac{2.3 \log (k_2/k_1)\, R}{(1/T_1) - (1/T_2)}. \tag{1.86}$$

LITERATURE

Butt, Yu. M. and Timashev, V. V., *Portland Cement Clinker*, Moscow, 1967.

Butt, Yu. M. and Timashev, V. V., *A Practical Course in the Chemical Technology of Binders*, Moscow, 1973.

Budnikov, P. P. and Ginstling, A. M., *Reactions in Blends of Solids*, 3rd revised and expanded edition, Moscow, 1971.

Instructions to the Laboratory Work "Kinetics of Dicalcium Silicate Formation"

1. Switch on the heating of the muffle and Silit kilns to burn specimens in the instructor's presence.

2. Prepare the mixture in accordance with the assignment.

3. Shape the mixture into specimens.

4. Place the specimens on the tray and insert them into the muffle preheated to 900-1000°C for 30 min.

5. Transfer the tray with the specimens into the Silit kiln at a predetermined temperature and withdraw them from the kiln at definite time intervals.

6. Take all the necessary precautions when working with high-temperature kilns; use specially designed stands and tongs to handle the hot specimens.

7. Do not heat and boil samples on an electric heater with an open coil. Cover it with a sheet of asbestos.

8. If organic solvents are used, heat them only in flasks coupled with reflux condensers.

LABORATORY WORK 7. COAL CARBONIZATION

Solid fuels are of paramount importance for the national economy. They are not only a source of energy but also raw materials for many industries. The by-product coke industry in our country supplies 67% of benzole, 100% of naphthalene, 100% of cresols, 90% of coumarone-indene resins and other essential compounds used in the manufacture of dyes, perfumes, medicines, tannins, and explosives.

The chemical processing of coal, shale, and peat (pyrolysis, gasification, hydrogenation, etc.) is the most rational way of utilizing these fuels. The most common of the above processes is pyrolysis (dry distillation), whereby a dry fuel is heated to high temperatures in the absence of air.

The pyrolysis of the organic mass of coal is a complex heterogeneous high-temperature process in which the reactions of decomposition yielding less complex substances are combined with those of condensation, that is polymerization and polycondensation of the decomposition products. The role and nature of individual concurrent and consecutive reactions with different activation energies are dissimilar in the process of pyrolysis of various types of solid fuels, however, the overall effect is endothermic as a rule; hence all kinds of pyrolysis require supply of heat. Pyrolysis is conducted in chamber ovens which are simple in design and ensure the required elevated temperatures.

As a result of heating of the coal charge, the energy of oscillatory molecular motion increases, the physical links between macromolecules weaken, and some chemical bonds break with gradual detachment of atomic groups which are energetically unstable at a particular temperature. The reactive radicals interact forming new compounds that exhibit different properties depending on the composition and structure of the raw material as well as process conditions. Thus, splitting of solid fuel macromolecules results in a carbonized solid phase (coke, low-temperature coke) and gas-vapour mixtures containing hydrocarbon gases and vapours.

Most of the reactions involved in pyrolysis of any kind of solid fuel are irreversible, that is the products of primary decomposition immediately enter into new reactions yielding other compounds, and the original compound cannot be formed again. Therefore, the end results of pyrolysis are to a great extent dependent on the ratio be-

tween the rates of the individual reactions. The primary and principal reaction of pyrolysis—thermal decomposition of macromolecules—is independent of pressure and is a function of temperature, according to the Arrhenius equation (1.37).

The most commonly applied process is coking which resides in slow heating of a coal charge in the absence of air up to 900-1000°C. The heating initiates a sequence of chemical, physicochemical, and chemical processes. For example, heating up to 200-250°C evaporates the moisture inherent in coal, giving rise to oxygen-containing gases (CO_2, CO). At about 300°C, gases, resin and water vapours (fuel decomposition products) start to evolve. In the neighbourhood of 350°C, the coal grains become coated with a film of liquid decomposition products. Further heating above 350°C brings coal to a liquid plastic state, and the viscosity of the mass gradually decreases.

At 500 to 550°C, the evolution of primary resin vapours and gas is maximum, then the plastic mass starts solidifying and forms low-temperature coke. At 700°C, polycondensation processes in the core portion of coal become predominant, and the low-temperature coke continues to decompose releasing hydrogen. At temperatures above 700°C, consolidation of coke takes place, while the primary gas-vapour mixture which comes in contact with the red-hot coke as well as walls and roof of the coking chamber enters into secondary pyrolysis reactions, ultimately yielding complex compounds containing gaseous products and substances of the aromatic series.

The industrial carbonization process comprises the following three main stages: (1) preparation of the coal charge and its loading into the coking chamber; (2) carbonization, extraction of the gas-vapour mixture, and discharging of coke; and (3) processing of the gas-vapour mixture. The last stage, in turn, includes five main steps: (a) cooling of the gas-vapour mixture with condensation and subsequent separation of the tar and tar water; (b) trapping of ammonia; (c) absorption of aromatic hydrocarbons (crude benzole), followed by their removal and separation; (d) deep freezing of the uncondensed gas and its fractionation; and (e) processing of the tar to obtain individual hydrocarbons of their blends.

The effect of the final process temperature on the yield of thermal decomposition products and the combustion heats of the end products (averaged values) are summarized below.

The lower calorific value of the high-temperature carbonization gas, as compared to that of the low-temperature carbonization one, stems from the higher hydrogen content in the former (usually 55 to 60% versus 15 to 20% in the latter) and the lower content of hydrocarbons.

Thus, the high-temperature carbonization gas contains 110 to 125 g/m³ of tar vapours, 35 to 42 g/m³ of benzole hydrocarbon vapours, 8 to 14 g/m³ of ammonia, 6 to 25 g/m³ of hydrogen sulphide, and up to 10 g/m³ of naphthalene.

	Low-temperature carbonization (500-600°C)	High-temperature carbonization (900-1000°C)
Solid residue (low-temperature coke or coke) yield, percentage of the coal charge	70-80	65-70
Tar yield, percentage of the coal charge	10-12	2.5-5.5
Gas yield, percentage of the coal charge	6-8	10-12
Gas yield per ton of charge, m³	60-80	300-350
Ammonia yield, percentage of the coal charge	trace amounts	0.1-0.35
Heat of gas combustion, kJ/m³	25 100-36 400	16 700-18 800

More than 200 various commercial products (300 and more grades) are obtained from the volatile products of carbonization.

The factors affecting the carbonization process and product yield include the coal charge composition, coal grain size, loading density, carbonization rate, and others. The coals most suitable for carbonization belong to grade C (coking). Since such coals are not mined in every coal field, a blend (charge) is prepared and thoroughly stirred. Coals must have a certain moisture content (5 to 8%) and contain a limited amount of ash and sulphur which convert to coke during carbonization, then adversely affect the smelting process in the blast furnace. If it is necessary to produce greater amounts of tar and gas, charges are prepared from coals with a high yield of volatile products (such as gas coals).

The smaller the grain size of the coal charge, the greater the viscosity of the plastic coal mass and the lower its swelling capacity. This can be explained by the greater amount of the liquid phase being used to wet the additional reactive surface formed as a result of finer crushing, as well as by partial oxidation of the coal as a result of oxygen adsorption by the surface additionally exposed during crushing. Fine crushing of coal increases the overall yield of gas and its hydrogen content.

Increasing the bulk weight of the coal charge not only enhances the capacity of coke ovens but also substantially improves the coke quality. To increase the bulk weight of the charge, solid (calcium oxide) and liquid hydrocarbon (kerosene, fuel oil) additives are introduced. Increasing the carbonization rate reduces the yield of metallurgical coke and raises that of coke in 60 to 25 mm sizes. At temperatures of up to 1000°C and above, the pyrolysis of the forming hydrocarbons intensifies, hence, the yield of tar decreases and that of gas increases.

The carbonization products and their properties are as follows:

coke—mechanically strong, porous (45—55%) material characterized by combustibility and high chemical activity. Coke sized in

excess of 25 mm (metallurgical coke) is used in blast furnaces. The volatile matter of the coking process consists of various gases, vapours of volatile liquids, and water vapours. Purified coke-oven gas containing 54 to 60% by weight of H_2, 20 to 25% by weight of CH_4, 5 to 7% by weight of CO, other hydrocarbons (heavier than methane) 2 to 3%, and so on is used in various chemical syntheses (ammonia, methanol, etc.), to intensify metallurgical processes, and as fuel;

tar—a dark brown viscous product containing more than 300 various chemical compounds, including benzene, toluene, xylene, phenols, cresol, naphthalene, anthracene, phenanthrene, pyridine, carbazole, coumarone, and others, many of which are isolated during subsequent processing and widely used in the chemical industry;

crude benzole—a blend of hydrogen sulphide, benzene, toluene, xylenes, coumarone, and some other compounds. Its distillation yields individual aromatics and mixed hydrocarbons.

Carbonization products are processed in several steps: condensation of tar and tar (ammonia) water from the gas-vapour mixture, trapping of ammonia, crude benzole, and hydrogen sulphide. Next comes processing of the tar and crude benzole to obtain individual chemical compounds or their mixtures. It involves many of the standard techniques and processes such as sorption, desorption, distillation, multiple rectification, and chemical reactions yielding new products. These processes are intensified and their rate increased primarily by varying temperature. Since most processes are conducted in a gas-liquid system, to extend the area of contact between the reacting phases use is made of packed towers (with counterflows of the gas and liquid), bubble columns, as well as sprinklers. Under laboratory conditions use can be made of a retort furnace if its heating coil can assure a temperature of at least 900°C.

This work is aimed at determining the yield (with drawing up of the material balance) of coke, tar, tar water, ammonia, crude benzole, uncondensed gases, and analyzing them.

Experimental Setup and Procedure

The process is conducted on a setup (Fig. 22) comprising a tube furnace *1* (1100 to 1200°C) mounted with a slight tilt (to facilitate the run-off of the tar), a quartz or porcelain tube *3* for carbonization (600 to 650 mm long and 20 to 30 mm in internal diameter) with a thermocouple *2* connected via a plug and a gas-discharge tube (12 to 16 mm in diameter) to a pressure gauge *4* and a trap *5* in a water bath, a calcium chloride tube *6*, absorption flasks *7* through *9*, two tubes *10* and *11* with activated charcoal, and a gas holder *16*. Another bent tube can be inserted between the trap *5* and calcium chloride tube *6* to prevent the tar residue from leaving the trap.

20 to 40 g of coal are thoroughly stirred, weighed on an analytical balance to within 0.0001 g, and carefully charged into the preweighed tilted (at 20 to 30°) carbonization tube *3*. Then, the tube is inserted into the furnace *1*, and the coal charge is levelled by means of a small poker so that the coal forms a uniform bed over that portion of the tube which is inside the furnace (but coming 4 to 6 cm short of the furnace end on either side). Since the coal tends to swell during carbonization and can block or narrow the exit of the gas-vapour
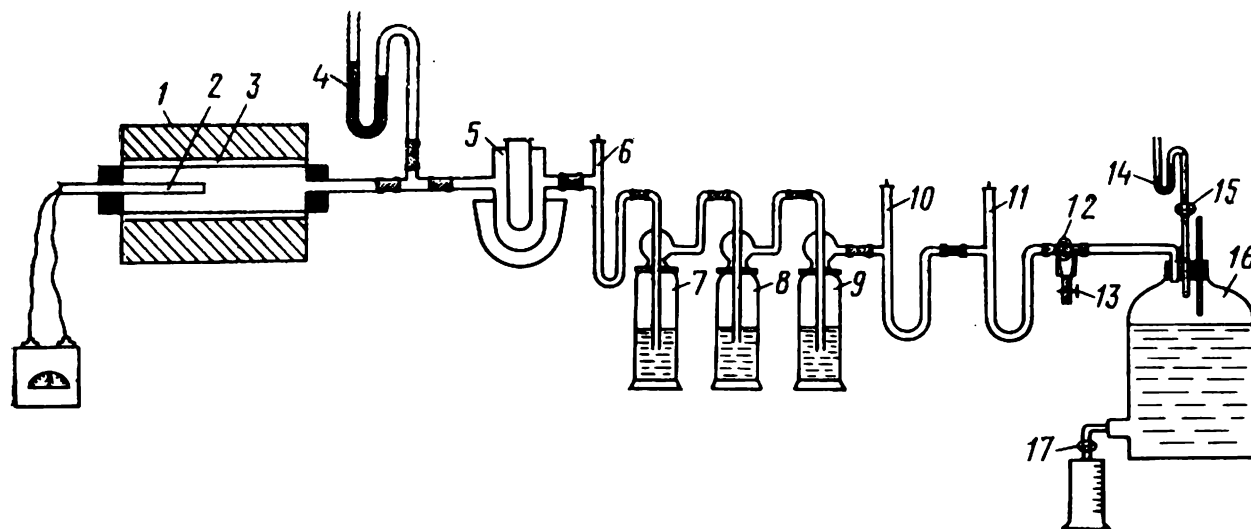
Fig. 22. Experimental setup for carbonization

mixture, the coal charge must be of a size not exceeding one third of the tube interior volume. The gas-discharge tube must be inserted into the plug as low as possible to avoid accumulation of the tar. The trap *5* serving as the tar and tar water condenser is filled with ice, snow, or an appropriate coolant and placed in the water bath that can be filled with cold water, ice, or snow. The calcium chloride tube *6* with properly roasted calcium chloride (grains 3 to 5 mm in size) is used to trap the remaining traces of moisture. The absorption flask *7* is charged with 10 to 20 cm^3 of 1 N H_2SO_4 (with methyl orange) to absorb ammonia, the flask *8* receives 30 to 40 cm^3 of a 30% NaOH solution to trap carbon dioxide and hydrogen sulphide, and the flask *9* is filled with 20 to 40 cm^3 of a mercuric oxide solution (41 g of mercuric oxide are dissolved in 200 cm^3 of 20% sulphuric acid) to trap unsaturated hydrocarbons. The two U-shaped tubes *10* and *11*, similar to the calcium chloride ones, are packed with predried activated charcoal to trap crude benzole*. All absorption

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* The used up activated charcoal is regenerated by driving off benzole with superheated steam, then the charcoal is baked in a muffle in the absence of air at 800°C for 8 hours. The regenerated charcoal is stored in a flask with a ground-glass stopper. The two U-shaped tubes with activated charcoal may be replaced by a column with a glass ring (or bead) packing, which is refluxed with coal-tar or straw oil, but in this case it is difficult to carry out accurate quantitative analysis of the trapped crude benzole.

flasks are weighed, after they have been filled with the absorbers, on an analytical balance to within 0.0001 g. The gas holder *16* is filled with a saturated NaCl solution.

After the setup has been assembled and tested for air-tightness*, the tube *3* with the coal charge is inserted into the tube furnace *1* preheated to a 100-110°C, followed by the thermocouple *2* (its end received by the tube must be approximately in the middle of the furnace), and the valve *17* on the gas holder *16* is immediately opened to let out the liquid seal from the latter. During the experiment, the pressure in the gauge *4* is maintained at 98 to 137.2 Pa by controlling the rate of the liquid seal flowing out of the gas holder. As a result, vacuum is created in the gas holder, sufficient to overcome the resistance of the entire absorption part of the system. After that, the valve *15* of the pressure gauge *14* mounted on the gas holder is opened. The heating that follows is performed at a rate of 5 to 10 deg/min up to 850-960°C, the final temperature being maintained for 30 to 40 minutes. Gas samples are taken by means of the cock *12* with a clamp *13*. Every 10 minutes, the following data are entered in the following table:

Time (hours and minutes)	Temperature, °C, of the		Pressure, Pa		Amount of gas in gas holder, cm3*	Remarks (visual examination)
	carbonization tube	gas in the gas holder	gauge, 4	gauge 14		

  * The amount of gas in the gas holder is determined with reference to the volume of the liquid seal flowing out of the latter.

By the end of the experiment, the pressure in the gas holder must be set at the atmospheric level by closing the valve *17* on the gas holder when the experiment is nearing completion. After exposure at 850 to 960°C (the final temperature and exposure time are specified by the instructor), the heating is stopped, all valves and cocks are closed, the tube *3* is disconnected from the thermocouple and absorption flasks, and the hot tube is put on a sheet of asbestos for cooling. The disconnection and cooling are performed so as not to lose coke particles. Finally, the absorption flasks are disconnected and weighed after staying open in air for at least 20 minutes (required for the residual gas, mainly hydrogen, to be displaced by air).

  * The setup is tested for air-tightness in the following manner: the carbonization tube *3* is tightly plugged, the pressure gauges *4* and *14* (the latter being on the gas holder) are disconnected by the valve *15*, and the valve *17* is opened letting the liquid seal out of the gas holder. If the setup is airtight, the liquid seal stops flowing out within a short period of time. Otherwise, the point of leakage must be found and the system rendered airtight.

Analytical Procedure and Calculation Examples

The cooled quartz tube is weighed to within 0.0001 g, and the additional weight will constitute the coke yield. Then, the coke is extracted from the tube by a wire hook (to be handed over to the laboratory assistant), the tube is reinserted into the furnace, and the coke particles stuck to the tube walls are burnt out at 700 to 800°C.

The additional weight of the trap *5* (Fig. 22) is contributed by the condensed tar and water. To determine the weight of the water, the trap contents are decanted into a round-bottomed flask *1* (Fig. 23), the trap is rinsed with 12 to 20 cm³ of xylene, and the washes are also transferred into the flask. The latter is coupled with a reflux condenser *3* and a collector, and the mixture is distilled. Xylene and water form an azeotropic mixture. The distillate is collected in the graduated receiver *2* till no more water is released. Its amount is easy to determine for a meniscus distinctly

Fig. 23. Condensate distillation unit

separates it from xylene. Added to this weight must be the additionally measured weight of the calcium chloride tube *6* (Fig. 22) that was absorbing the vapours of the water released during the experiment.

Example of Product Yield Calculation. Calculate the yield of ammonia, CO_2, H_2S, unsaturated hydrocarbons, crude benzole, and gas (per kg of the starting coal), if the coal charge weighs 25 g.

Solution. 16 cm³ of 1 N H_2SO_4 were taken before the experiment; 10.3 cm³ of 1 N alkali were spent in back titration after the experiment, and 16—10.3 = = 5.7 cm³ of the acid were spent to neutralize ammonia. Hence, the yield of ammonia is

$$5.7 \cdot 0.01\ 768 \cdot 100/25 = 5.7 \cdot 0.01\ 768 \cdot 4 = 0.403\%,$$

where 0.01 768 is the titre of sulphuric acid with respect to ammonia and 25 is the coal charge, in g.

The additional weight of the absorption flask *8* (see Fig. 22) after the experiment corresponds to the yield of the carbon dioxide and hydrogen sulphide mixture. Students may be told to determine these gases separately. In that case, the alkaline solution is poured, after weighing, into a measuring flask having a capacity of 250 cm³, the absorption flask is rinsed two or three times with distilled water which is poured into the same measuring flask, the solution being made up with water to the mark.

Then, 50 cm³ of distilled water acidulated with hydrochloric acid are poured into a 250-cm³ conical flask, 10 to 30 cm³ (depending on the sulphur content in the coal) of a 0.1 N iodine solution are added, and 25 cm³ of the solution pipetted from the measuring flask are dropped with stirring. The unreacted excess iodine is titrated with 0.1 N $Na_2S_2O_3$. The yield of hydrogen

sulphide is determined as follows. Let the additional weight of the absorption flask *8* be 0.284 g after the experiment; 26.2 cm³ of a 0.1 *N* iodine solution are taken, and 14.1 cm³ of 0.1 *N* Na₂S₂O₃ are spent in the back titration.

Hence, hydrogen sulphide has combined with 26.2 — 14.1 = 12.1 cm³ of iodine. This gives the amount of hydrogen sulphide

$$(12.1 \cdot 0.001703 \cdot 250)/25 = 0.2061 \text{ g,}$$

or

$$0.2061 \cdot 100/25 = 0.2061 \cdot 4 = 0.824\%.$$

Then, the yield of carbon dioxide is

$$0.284 — 0.2061 = 0.0779 \text{ g,}$$

or

$$0.0779 \cdot 100/25 = 0.0779 \cdot 4 = 0.3116\%.$$

The yield of unsaturated hydrocarbons is determined from the weight of the absorption flask *9* (see Fig. 22) after the experiment, and that of crude benzole is determined from the weight of the U-shaped tubes *10* and *11* with activated charcoal. After weighing, the activated charcoal from the first U-shaped tube along the flow of the gas-vapour mixture is taken for regeneration, the tube is packed with fresh activated charcoal, and in the next experiment this tube becomes the second, while the first one is the tube which was the second in the previous experiment.

After the above determinations have been made, a gas sample is taken for analysis from the gas holder. The assignment may include determination of the gas density as well. To sample the gas from the gas holder, an overhead bottle with a liquid seal is connected through a hose to the pipe with the pinch cock *17*. The entire system is disconnected by means of the three-way cock *12* and connected to a gas analyzer. The head bottle is raised above the level of the liquid seal in the gas holder, the valves *17* and *13* are opened, then the cock *12*, and the gas is fed into the gas analyzer. This is how the gas is analyzed at the end of the work. If the instructor gives an assignment to perform analysis in the course of carbonization, the gas holder *16* is disconnected by means of the cock *12*, and the gas is directed into the gas analyzer. The gas yield is found as follows. Let the amount of gas at the end of the experiment be 7.9 dm³. Then, its yield per kg of the coal is

$$7.9 \cdot 100/25 = 316 \text{ dm}^3,$$

or 316 m³ per ton of the coal.

The gas volume under normal conditions is recalculated using the formula

$$V_0 = V (B — p) 273/(273 + t) 760, \qquad (1.88)$$

where V_0 is the gas volume under normal conditions, in dm³; V is the gas volume under the experimental conditions, in dm³; p is the water vapour pressure at a particular temperature of the gas (Table 1*), in Pa; t is the gas temperature, in °C; and B is the barometric pressure, in Pa. The gas analysis is based on one of the methods described in Work 36 or chromatographically (Work 37).

At the end of the experiment, the material balance per ton of the coal charge is drawn up, and the disbalance is calculated as follows:

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* Table 1 lists the partial pressure and weight of water vapours at different temperatures (at complete saturation of the gas and at atmospheric pressure).

In			Out			
Item	Amount		Item	Amount		
	kg	%		kg	%	m³
Coal charge	1000	100	Coke Tar Water Ammonia Hydrogen sulphide Carbon dioxide Crude benzole Gas			

Table 1

Tempera-ture, °C	Pressure 133, Pa	Water vapor content per m³, g	Tempera-ture, °C	Pressure 133, Pa	Water vapor content per m³, g
13.0	11.23	11.38	16.6	14.17	14.15
13.1	11.30	11.44	16.7	14.26	14.23
13.2	11.38	11.51	16.8	14.35	14.32
13.3	11.45	11.57	16.9	14.44	14.40
13.4	11.53	11.64	17.0	14.53	14.49
13.5	11.60	11.71	17.1	14.62	14.57
13.6	11.68	11.78	17.2	14.71	14.66
13.7	11.76	11.85	17.3	14.81	14.74
13.8	11.83	11.91	17.4	14.90	14.83
13.9	11.91	11.98	17.5	15.00	14.92
14.0	11.99	12.05	17.6	15.09	15.01
14.1	12.06	12.12	17.7	15.19	15.09
14.2	12.14	12.20	17.8	15.28	15.18
14.3	12.22	12.28	17.9	15.38	15.27
14.4	12.30	12.36	18.0	15.48	15.36
14.5	12.38	12.43	18.1	15.57	15.45
14.6	12.46	12.51	18.2	15.67	15.54
14.7	12.54	12.59	18.3	15.77	15.63
14.8	12.62	12.67	18.4	15.87	15.73
14.9	12.71	12.75	18.5	15.98	15.83
15.0	12.79	12.83	18.6	16.07	15.91
15.1	12.87	12.91	18.7	16.17	16.00
15.2	12.95	12.99	18.8	16.27	16.10
15.3	13.04	13.07	18.9	16.37	16.19
15.4	13.12	13.16	19.0	16.48	16.29
15.5	13.20	13.24	19.1	16.58	16.39
15.6	13.29	13.32	19.2	16.68	16.49
15.7	13.37	13.40	19.3	16.79	16.59
15.8	13.46	13.48	19.4	16.89	16.69
15.9	13.55	13.57	19.5	17.00	16.79
16.0	13.63	13.66	19.6	17.10	16.89
16.1	13.72	13.74	19.7	17.21	16.99
16.2	13.81	13.82	19.8	17.32	17.09
16.3	13.90	13.90	19.9	17.43	17.29
16.4	13.99	13.99	20.0	17.53	17.39
16.5	14.08	14.07			

Note: The amounts of hydrogen sulphide, carbon dioxide, and unsaturated carbons for the material balance per ton of the coal are calculated as follows:

$$H_2S = 0.824 \cdot 10/1.521 = 5.42 \ m^3/t,$$
$$CO_2 = 0.3116 \cdot 10/1.966 = 1.59 \ m^3/t,$$
$$C_mH_n = x10/1.490 \ m^3/t,$$

where 1.521, 1.966, and 1.490 stand for the weight of 1 dm^3 of H_2S, CO_2, and C_mH_n, respectively, and x is the percentage yield of C_mH_n as a result of the experiment.

The instructor may assign determination of the coke-oven tar density and viscosity.

LITERATURE

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Instructions to the Laboratory Work "Coal Carbonization"

1. Make sure that the carbonization tube is clean, fill all the absorption flasks, and weigh them to within 0.0001 g.

2. Thoroughly stir the coal charge, weigh it, and load into the preweighed carbonization tube.

3. Assemble the experimental setup (by joining the components in series with the aid of flexible rubber hoses) and test it for air-tightness.

4. Insert the tube into the furnace (preheated to 100-110°C), then the thermocouple. Heat the tube at a rate of 5 to 10 deg/min to the desired temperature.

5. During the experiment, maintain the pressure at the gauge within the range of 100 to 150 Pa.

6. After holding the tube with the coke at the final temperature, withdraw it from the furnace and put it on an asbestos sheet for cooling.

7. To avoid blow-out, distill the tar and water with the aid of xylene by careful heating (by appropriate manipulation of the burner).

8. During the experiment, record the temperature, pressure, and the amount of gas in the gas holder every 10 minutes (see p. 87).

9. Regenerate the spent activated charcoal from the first U-shaped tube along the gas flow by driving off benzole with superheated steam, then give it to the laboratory assistant for baking.

10. After weighing the tube with the coke, extract the latter and reinsert the tube open at both ends into the furnace to burn off the coke particles stuck to the tube walls at 700 to 800°C.

11. Carry out all calculations, including the material balance, from the results of at least two simultaneous analyses, provided they are in agreement.

LABORATORY WORK 8. LOW-TEMPERATURE CARBONIZATION

Low-temperature carbonization is a process in which a solid fuel is pyrolyzed in the absence of air with the temperature being raised to 500-600°C. Just as every pyrolysis of the organic mass of a solid fuel, low-temperature carbonization is a complex heterogeneous process with decomposition reactions yielding simpler compounds

proceeding concurrently with those of condensation, that is polymer-ization and polycondensation of the decomposition products.

Low-temperature coke is a brittle material or noncaking powder differing from coke by a higher content of volatile matter (up to 10%) and greater reactivity. As compared to the starting material, low-temperature coke contains more carbon and ash but less oxygen and hydrogen. The high porosity of low-temperature coke is respon-sible for its low bulk weight.

The combustion heat of low-temperature coke changes but insigni-ficantly, when compared to the coal charge. In some cases it even decreases, presumably because of the lower hydrogen content. Because of the low strength and tendency to spontaneous combustion, low-temperature coke is not transportable. Therefore, the most rational way to utilize low-temperature coke is to burn it on the production site as power- or gas-generating fuel. Sometimes low-temperature coke is used as an inert component of the charge in high-temperature carbonization to enhance the yield and quality of coke. In recent years, it has become standard practice to briquette the low-temper-ature coke breeze in view of the broader applicability of briquettes as compared with the normally produced lump low-temperature coke.

The calorific power of the primary gas (the gas yield is 60 to 110 m^3 per ton of the processed coal) ranges from 25 100 to 36 400 kJ/m^3 because of the high content of methane and its homologues. Such gas can be used for municipal (town gas) or industrial purposes. Hydrogen, methane, or olefines can be used at chemical plants for synthesis of ammonia, alcohols, and other compounds. The gas-vapour mixture resulting from low-temperature carbonization serves as a source of tar, which is separated by cooling, or low-boiling hydro-carbons, which are isolated by oil washing, the latter yielding, after distillation and condensation, gas petrol (50 to 80 g per cubic metre of the gas) similar to refinery petrol.

Primary tar is one of the most valuable products of low-temper-ature carbonization. It is a dark brown liquid containing, primarily, compounds of the saturated, unsaturated, and naphthene series, higher phenols, and the like. Tar is processed into petrol, kerosene, lubricating oils, paraffin wax, and other products. It is separated by distillation into several fractions which are essentially blends of various hydrocarbons. To increase the yield of light fractions, the heavy residue is subjected to cracking or hydrogenation, whereby synthetic fuel is produced. A major effect on the composition and amount of the products is produced by the secondary decomposition reactions occurring as the gas leaves the low-temperature carboni-zation zone.

Low-temperature carbonization is carried out in directly or indi-rectly fired ovens of various designs—vertical and horizontal (shaft and tunnel), rotating, stationary, and so on. Particularly promising

is low-temperature carbonization of small solid fuel in a fluidized bed. The process comprises the following basic steps: (1) preparation of the raw material (coal, peat, shale), including crushing, sizing (sometimes briquetting) and loading into the oven for low-temperature carbonization; (2) low-temperature carbonization; (3) cooling of the gas-vapour mixture and condensation of the tar vapours; and (4) dehydration of the crude tar and its fractionization with subsequent refining of the fractions.

The low-temperature carbonization process and product yield are affected by a number of factors, such as temperature, fuel lump size, pressure, composition of the raw material, and others.

1. Effect of Temperature. Initially, the thermal decomposition of the fuel depends on its chemical composition and is characterized by release of gas and tar. At temperatures ranging from 100 to 250°C, the hygroscopic water is removed, and oxygen-containing gases (CO, CO_2) are formed. The temperature at which tar starts to evolve is in the neighbourhood of 300°C. At the same time, a sizable amount of water known as decomposition or pyrogenic water is formed. At 350 to 500°C, the evolution of the primary tar intensifies. Most of the volatile fuel components are driven off at temperatures of up to 500-550°C. The content of volatile matter in low-temperature coke varies from 9 to 20%.

The fuel heating may be slow or fast. In the case of slow heating, the decomposition products are removed from the process zone before they undergo secondary decomposition, which not only ensures a high yield of liquid products but also improves their quality. When heated fast, the decomposition products have no time to leave the low-temperature carbonization zone and are partially cracked with the result that the yield of gas increases at the expense of the liquid products and the quality of the latter gets worse.

2. Effect of the Fuel Lump Size on the Product Yield. The yield of low-temperature carbonization products is strongly affected by the lump size of the solid fuel loaded into the furnace. The smaller the fuel lump size, the greater the tar yield and, vice versa, the larger the lumps, the greater the yield of low-temperature coke and gaseous products (Table 2).

Table 2

Fuel lump size, mm	Percentage yield		Content of volatile substances in low-temperature coke, %
	primary tar	low-temperature coke	
20-30	10.3	41.4	8.8
100-120	8.1	45.5	10.3

Because of the poor heat conductivity of coal, individual lumps are heated on the surface to a much greater extent than inside, and the larger the lumps, the greater the temperature difference. As gases and tar vapours pass through the surface layers of the fuel lumps at a higher temperature, they decompose releasing simpler hydrocarbons.

3. **Effect of Pressure on the Product Yield.** An increase in pressure slightly increases the yield of low-temperature coke and gas, while the yield of tar decreases. Table 3 shows the yield of low-temperature coal carbonization products at different pressures.

Table 3

Pressure, Pa	Distillation products, %		
	low-temperature coke	primary tar	gas + losses
$1 \cdot 10^5$	67.3	13.0	7.7
$5 \cdot 10^5$	68.8	7.9	11.6
$25 \cdot 10^5$	71.0	5.1	11.5
$50 \cdot 10^5$	72.0	3.8	12.6

At 5.0 MPa and higher pressures, the process yields adequately caked low-temperature coke of higher strength. In low-temperature coke ovens designed specially to produce high-strength coke, the pressure inside the coal charge is raised artificially.

4. **Effect of the Raw Material Composition.** The yield and quality of low-temperature carbonization products depend on the composition of the raw solid fuel. The gas yield and composition resulting from low-temperature carbonization of different grades of coal at 525°C are listed in Table 4.

Table 4

Coal	Gas yield, m³/t	Gas composition, %						
		CO_2	C_mH_n	O_2	CO	H_2	C_mH_{n+2}	N_2
Grade PZh (Donets Basin)	117	6.5	3.9	0.6	3.0	13.8	68.0	4.2
Grade G (Donets Basin)	58	8.6	5.1	0.5	4.4	12.5	61.6	7.2

As can be seen from Table 4, the yield and composition of gaseous products of low-temperature carbonization vary widely depending on the coal composition.

At the same time, the average composition of the primary gas evolved during low-temperature carbonization varies, all other things being equal, as function of temperature (Table 5). As a rule, the

Table 5

Temperature, °C	Content, %						
	CO_2	CO	C_mH_n	CH_4	C_2H_6	H_2	N_2
420	15.5	8.4	9.5	33.6	17.0	10.4	5.6
500	6.2	6.2	4.6	40.3	12.8	24.8	5.7
> 500	5.0	5.2	2.2	41.4	6.2	34.0	6.2

higher the oxygen content in the fuel, the greater the primary tar yield. The greatest amount of tar is yielded by sapropelites. Humic coals yield tars with a high content of phenols (25 to 50%). The low-temperature carbonization of sapropelic coals yields phenol-free resins (up to 60%).

Peat lends itself more readily to low-temperature carbonization than coal. In this case, even at 170°C and above the process starts yielding tar (peat tar) which then can be processed into waxes, paraffins, pitch, and some other products. The low-temperature peat coke is used as a reducing agent in gasification, activated charcoal production, and other processes. Tar water is used as a source of acetic acid and phenols.

When Estonian shales are carbonized, the tar yield (with respect to the shale charge) is about 34% and that of gas is about 10%. The shale tar resulting from low-temperature carbonization can be distilled to yield benzene, ligroin, kerosene, diesel-fuel fractions, and residue. It contains 20% and more of phenols—a valuable raw material for the chemical industry.

The gas produced by low-temperature carbonization of Estonian shales approximately has the following composition (% by volume): CO_2—21.0; H_2S—7.0; CO—6.0; CH_4—31 to 32; unsaturated hydrocarbons—29 to 30; and H_2—4.0. Fractionation of such gas yields, after removal of hydrogen sulphide, valuable unsaturated hydrocarbons (ethylene, propylene) for chemical syntheses. Because of the high ash content in the charge, low-temperature shale coke contains roughly 10% of carbon, the balance being such mineral substances as calcium oxide, silica, and others. In ovens heated internally by an inert gas, the volatile products are easier to remove, hence, their yield is improved.

It is the purpose of this work to determine the yield of primary products of low-temperature carbonization (material balance) and analyze them.

Experimental Setup and Procedure

The low-temperature carbonization product yield is determined in a standard aluminium retort. It permits rapid and accurate reproduction of the process as well as determination of the yield of low-temperature coke, primary tar, tar water, and gas. The low-temperature carbonization of solid fuels in a laboratory is carried out either in a standard retort or in a modified one.

The modified retort is a thick vessel made of metal (Fig. 24), characterized by high thermal conductivity which ensures its uniform
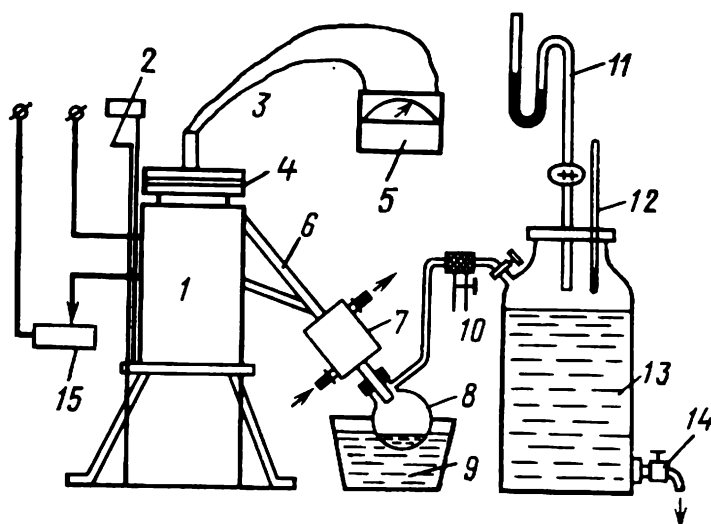
Fig. 24. Experimental setup for low-temperature carbonization:

1—retort; *2*—spring-loaded retort handle; *3*—thermocouple; *4*—retort cover; *5*—galvanometer; *6*—discharge tube; *7*—condenser; *8*—flask; *9*—vessel with cooling water; *10*—three-way pinchcock; *11*—pressure gauge; *12*—thermometer; *13*—gas holder; *14*—gas holder cock; *15*—rheostat

heating (in all of its parts) so that the primary distillation products are not overheated and do not decompose. The retort is tightly (with the aid of special clamps) closed from above with a cover having an asbestos lining and is provided with an oblique metal tube (12 to 14 mm in internal diameter) which passes through a water cooler and is intended to remove the gas-vapour products of low-temperature carbonization. The retort is also provided with a spring-loaded handle permitting the retort to be tilted for loading the charge and extracting the formed low-temperature coke. The setup must first be tested for air-tightness. The results of laboratory experiments are slightly at variance with the actual process parameters, however, they are sufficiently reliable for comparison of various types of mineral fuels insofar as their composition and importance for different distillation processes are concerned.

The retort is loaded with 40 to 75 g of crushed fuel, such as coal (up to 0.07 mm in size), shale, and others, after which the cover is tightly closed with the aid of the clamps. The charge is weighed to within 0.01 g. The temperature is measured by a thermocouple

inserted into a special holder in the retort cover and by a galvano-
meter. The metal tube is inserted into the stopper of a preweighed
flask with a discharge tube immersed into a cooling mixture. The
flask is coupled to the tube of the retort so that the end of the latter
enters the flared part of the flask without touching its walls. The
retort is heated to 500-510°C electrically, the temperature and heating
rate being controlled by a rheostat *15*. The heating program is such
that within the first 10 to 15 minutes the temperature in the retort
reaches 250-260°C, then, every subsequent 6 to 12 minutes, it is
raised by 50° to the preset level.

The gas-vapour mixture evolving in the course of heating is sup-
plied through the discharge tube and the condenser into the flask
in which the tar and water are condensed, while the uncondensed
gases flow further into a gas holder; the outflow of the liquid seal
is controlled by means of the cock so as to maintain the gauge pres-
sure constant (2.2 to 4.4 Pa). The heating continues till no more
tar drops are produced. The appearance of the first tar drop marks
the onset of the low-temperature carbonization process, the end
of the process coinciding with the last drop.

To determine the amount of the tar water released during low-
temperature carbonization, added to the flask with the distillate
after it has been weighed again are 20 to 45 cm³ of xylene which
forms an azeotropic mixture with water. The contents are transfer-
red into a round-bottomed flask, a few capillaries or pieces of pumice
are thrown into it, and the flask is coupled to a reflux condenser
and a collector. The mixture is distilled. The distillate is collected
into a graduated receiver till no more water is released. The amount
of water is easily determined for it is separated from xylene by
a clearly defined meniscus. The low-temperature coke remaining
in the retort is withdrawn and weighed to within 0.01 g. To this end,
the retort is tripped by means of the spring-loaded handle, and the
coke is discharged onto a special tray.

The amount of the evolved gas which is collected in the gas holder
or vented into the exhaust hood is determined from the difference
between the weight of the coal charge and the total weight of tar,
pyrogenic water, and low-temperature coke. If all of the gas is col-
lected in the precalibrated gas holder, the volume of the evolved
gas is simply measured. 10 to 15 minutes (according to the assign-
ment) after the gas started to evolve intensively, it is sampled for
analysis by means of the three-way pinchcock. Connected to the
latter is a small gas holder filled to the brim with a saturated NaCl
solution. The lower cock is opened for the liquid to flow out dropwise
from the gas holder, whereby the gas sample is forced into the latter.

The gas evolved during low-temperature carbonization is analyzed
using one of the methods described in Work 36 or chromatograph-
ically (see Work 37).

After the heating of the retort is over, the pressure gauge is disconnected from the gas holder by a valve, and the cock of the gas holder is closed at the same time. Then, the volume of the liquid that has flown out of the gas holder is measured, the gas temperature is measured by a thermometer, the final measurement being that of the barometric pressure. The gas volume is recalculated for normal conditions (0°C and $1.01 \cdot 10^5$ Pa), using Eq. (1.88), and the yield of gas is determined in a similar fashion. The results are used to draw up the material balance per ton of the fuel, then the disbalance is calculated.

LITERATURE

State Standard GOST 6382-75. Lignite, Coal, and Anthracite. Methods for Determining the Yield of Volatile Matter.

Instructions to the Laboratory Work "Low-Temperature Carbonization"

1. Make sure that the retort is clean, assemble the experimental setup, load the necessary amount of solid fuel, close the retort tightly, and test the entire setup together with the instructor.
2. Place the retort so as to avoid contact between its terminals and metal objects.
3. Switch on the heating of the retort and activate the condenser (for condensation of the emerging vapours).
4. After the process is over and the retort has cooled a little, open the cover (only using gloves). After the retort has cooled completely, discharge the contents onto the tray by tilting the retort with the aid of the spring-loaded handle.
5. Distill tar and water by careful heating (by properly manipulating the burner).
6. Be careful when handling the bromine water releasing bromine vapour during the gas analysis and determination of unsaturated hydrocarbons.

LABORATORY WORK 9. PYROLYSIS OF PETROLEUM PRODUCTS

At present, a great variety of techniques for refining petroleum and petroleum products are widely used, including thermal and catalytic cracking of distillates and fuel oils.

The cracking of petroleum products is performed to produce light hydrocarbons from heavier ones, primarily for petrol.

The high-temperature cracking (670-720°C) of crude oil, known as pyrolysis, is intended to yield gases subsequently used as the starting material in organic synthesis, including synthesis of high-octane components of motor fuel, and various liquid products with a high content of aromatics. In terms of temperature, pyrolysis is the most rigorous form of thermal cracking, being characterized by a more complete decomposition of the hydrocarbons present in crude oil. Most reactions involved in pyrolysis are irreversible as a rule, that is the primary decomposition products immediately undergo further conversion and are not capable of forming the initial sub-

stance. Thus, the pyrolysis of liquid hydrocarbons is a polyphase high-temperature process in which the decomposition of the starting hydrocarbons occurs in a homogeneous medium, resulting in gas, liquid and solid phases (coke, carbon black). The following are the factors influencing the pyrolysis process and product yield.

1. Raw Material. The pyrolysis rate and products depend on the properties of particular hydrocarbons present in the raw material, including the molecular weight and the conditions under which the process is conducted. The higher the molecular weight, the lower the thermal stability of all hydrocarbons, the stablest of all being such low-molecular compounds as methane, ethane, benzene, toluene, and others. Light starting hydrocarbons yield large amounts of gas, whereas the pyrolysis of heavy stock yields a greater amount of aromatics and liquid olefines. Hence, the raw material is selected, primarily, depending on the end products of pyrolysis.

2. Pyrolysis Temperature. Of all petroleum hydrocarbons and products the lowest thermodynamic stability is exhibited by paraffin hydrocarbons, while aromatic hydrocarbons are the most thermodynamically stable; olefine and naphthene hydrocarbons occupy an intermediate position. As the temperature rises, the docomposition rate of saturated hydrocarbons increases faster than that of other hydrocarbons, the decomposition usually occurring in the middle of the molecule and yielding paraffins and olefines of a lower molecular weight:

$$C_{m+n}H_{2(m+n)+2} \rightarrow C_mH_{2m} + C_nH_{2n+2}$$

For example,

$$C_{16}H_{34} \rightarrow C_8H_{18} + C_8H_{16}$$
$$\text{solid} \qquad \text{liquid} \qquad \text{liquid}$$
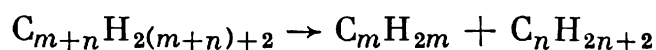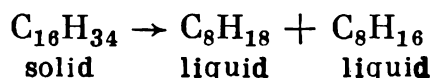
The resulting lighter saturated hydrocarbons may break down in the same manner into still simpler molecules. The unsaturated hydrocarbons forming at elevated temperatures in vapour-phase cracking, particularly in pyrolysis, undergo structural changes and regroup into cyclic hydrocarbons—naphthenes. For example,

$$CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2 \rightarrow
\begin{array}{c}
CH_2 \\
\diagup \quad \diagdown \\
H_2C \qquad CH_2 \\
| \qquad \quad | \\
H_2C{-}\!\!-\!\!{-}CH_2
\end{array}$$
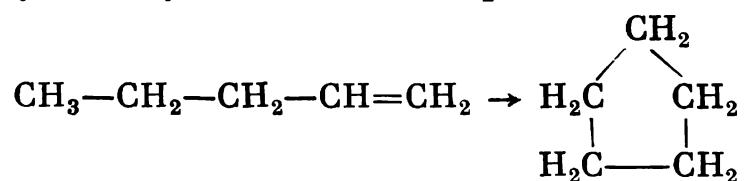
Being dehydrogenated at the high temperature (720 to 750°C) of pyrolysis, naphthenes convert to hydrocarbons of the aromatic series. For example,

$$
\begin{array}{c}
CH_2{-}CH_2 \\
\diagup \qquad \diagdown \\
H_2C \qquad \qquad CH_2 \\
\diagdown \qquad \qquad \diagup \\
CH_2{-}CH_2
\end{array}
\rightarrow 3H_2 +
\begin{array}{c}
CH \\
\diagup \quad \diagdown\!\!\!\diagdown \\
HC \qquad CH \\
|| \qquad \quad | \\
HC \qquad CH \\
\diagdown \qquad \diagup\!\!\!\diagup \\
CH
\end{array}
$$
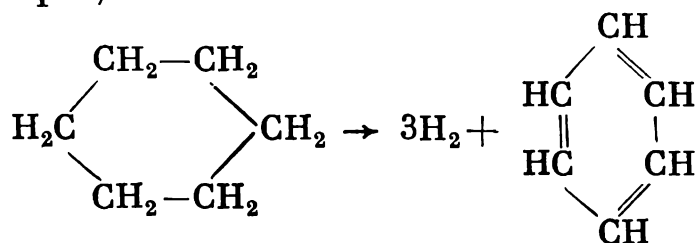
The gaseous pyrolysis products contain unsaturated hydrocarbons of the olefinic and diolefinic series, saturated hydrocarbons, and hydrogen. The yield of gaseous products is 45% and that of liquid products is 50%. The liquid products contain a large amount of aromatic hydrocarbons which are constituent components of the liquid oil produced through distillation of the pyrolysis tar. The optimal temperature of pyrolysis is 670 to 720°C. Pyrolysis at lower temperatures yield more xylene. The yield of benzene increases up to 750°C, then remains almost constant. The toluene yield reaches a maximum at 700°C, then decreases as the temperature continues to rise. At temperatures above or below the optimum, the yield of aromatics decreases and the ratio between the latter changes. Hence, to each temperature there corresponds an optimal contact time at which the amount of the end product is maximum.

3. Pyrolysis Time. Increasing the time of residence of the stock in the reaction zone enhances the yield of aromatic hydrocarbons. As a rule, the reactions involved in pyrolysis are irreversible. The basic reaction—thermal decomposition—is normally regarded as a homogeneous noncatalytic monomolecular first-order reaction proceeding in the gas phase. The rate constant is a function of temperature according to Eq. (1.86). The rate of thermal decomposition reactions obeys the following first-order equation

$$u_A = k_v C_A, \qquad (1.89)$$

in which k_v is the reaction rate constant at a constant volume and C_A is the concentration of component A.

Eq. (1.89) can also be written as

$$u_A = k_p P_A, \qquad (1.90)$$

where k_p is the reaction rate constant at constant pressure and P_A is the partial pressure of component A.

The pyrolysis tar composition depends, mainly, on the process temperature and contact time. The quality of the stock produces practically no effect on the composition of the liquid products. The distillation of the pyrolysis stock may yield the following fractions (Table 6).

Table 6

Fractions	Boiling point, °C	Density, g/cm³
Light oil	170	0.845-0.870
Naphthalene oil	170-240	0.900
Scrubbing oil	240-300	0.950

The yield of light oil is normally 40 to 45% of the tar weight or 20 to 25% of the stock weight. The rectification of light oil yields benzene, toluene, and xylene, their total yield exceeding 10% of the stock weight. To remove unsaturated hydrocarbons, the benzene and toluene fractions are cleaned with 92% sulphuric acid, washed with water then an alkali, and subjected to secondary rectification with particular aromatics being taken off within narrow temperature intervals. 50 to 60% of the light fraction are constituted by unsaturated compounds, chiefly amylenes and hexylenes (starting materials in the production of respective alcohols). The side-cut distillates resulting from separation of benzene and toluene and containing many unsaturated and aromatic compounds are good high-octane additives to motor fuel, improving its quality.

The fraction boiling at a temperature above 112°C serves as a solvent. The naphthalene fraction is processed into naphthalene. The coke yielded by the pyrolysis tar pitch is used in the manufacture of electrodes and high-quality steel. Ethylene, which forms the major part of the gas evolved during pyrolysis, is adequately purified and goes into the production of polyethylene, ethanol, dichloroethane, and other compounds.

This work is aimed at determining the yield of pyrolysis products depending on the type of raw material, process temperature, and stock feed rate, as well as analyzing the products.

Experimental Setup and Procedure

The laboratory setup for pyrolysis of petroleum products is shown schematically in Fig. 25. The starting material is fed into the furnace *3* by a 200-300-cm³ burette *1* filled before the experiment. The stopcock of the burette is calibrated to a particular feed rate. The burette communicates with the furnace via a glass and a metal tube. Pyrolysis is conducted in a metal (or quartz) tube 750 to 850 mm long and 20 to 35 mm in diameter, inserted into the electrically heated and asbestos-insulated cylindrical furnace. The furnace has blank flanges, welded to one of which is a stock feed tube *2* and to the other, a holder *4* for the thermocouple *5* connected to a galvanometer *6*. The pyrolysis products are discharged through the tube *7* extending from the lower portion of the furnace slightly tilted toward the receiver *8* in which most of the liquid pyrolysis products are condensed. The uncondensed lighter fractions enter the receiver *9* coupled via a reflux condenser *10* to the absorption flask *11* filled with absorption oil. Before the experiment, the receivers *8*, *9*, and absorption flask *11* are weighed to within 0.01 g.

A pressure gauge *12* is provided to measure the pressure in the system. The yield of gaseous products of pyrolysis is measured with the aid of the gas holder *13* connected to a water-jet pump *17*. During

the experiment, at definite time intervals (every 15 to 20 minutes), gas is sampled into the gas holder *16* with the aid of a three-way cock *15*. The stock is analyzed for aromatics content. The temperature in the furnace is maintained constant by means of a rheostat.

Since the depth of decomposition during pyrolysis depends on the process temperature and the time of residence of vapours in the furnace, the optimal rate of feeding the starting substances into the laboratory furnace at a given temperature must be determined experimentally. For instance, at 650 to 700°C, the furnace being about 0.8 m long and 30 mm in diameter, the stock feed rate may
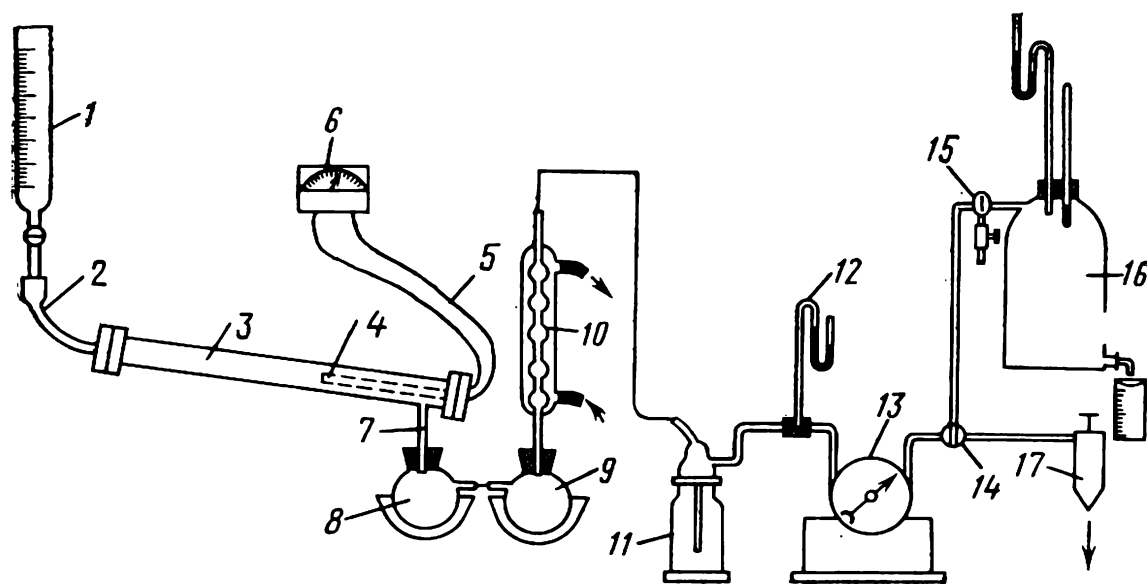
Fig. 25. Experimental setup for pyrolysis of petroleum products

vary from 1 to 2 cm³/min to provide for a maximum yield of aromatics. Thus, in carrying out the assignment, the effect of the above factors on the process results must be taken into consideration. The duration of the experiment at this stock feed rate is selected such as to yield pyrolysis products in an amount sufficient for their analysis. For example, when 0.25 to 0.3 dm³ of the starting materials are processed during the experiment, the amount of the pyrolysis products is quite sufficient, that is, at a feed rate of 2 cm³/min, the experiment will last 2 to 3 hours.

Pyrolysis on the above-described setup will produce good results if the following conditions are met: (1) starting substance—kerosene; (2) experimental temperature—700 to 720°C; (3) kerosene feed rate—1 to 2 cm³/min; and (4) duration of the experiment—2 to 3 hours. After the experiment, the yields of the main primary products are determined.

According to the assignment, a gas sample may be taken during pyrolysis with the aid of the valve *15* for determination of unsaturated hydrocarbons by bromination and saturated hydrocarbons

by burning the sample in the gas analyzer. The gas holder is connected as follows: the nose for the gas emerging from the furnace is connected to the nipple on the rear cover of the gas holder, while the gas from the latter flows via the valve *14* toward the water-jet pump, through a hose fitted on the nipple on top of the gas holder. To ensure high accuracy of measurement, the pressure and temperature of the gas and water in the gas holder must be taken into account during the experiment (if the instructor tells so). Then, the pressure and temperature are measured in the course of the experiment at hourly intervals. For these measurements, two holes are provided on top the gas holder: one for connection of a U-tube manometer and the other to receive a thermometer for measuring the gas temperature.

Located in the bottom portion of the gas holder is a cock to drain the water. (The gas holder is to be installed and connected by a student under the supervision of the instructor or chief laboratory assistant.)

Once the desired temperature is reached, the water-jet pump is started, and the starting substance is fed into the furnace for pyrolysis. The absorption flask *11* may be replaced by an absorption column with glass packing, refluxed from the top (with absorption oil) in a counterflow with respect to the supplied gas. However, with such an arrangement it is more difficult to draw up the material balance for it is impossible to measure at the end of the experiment, the oil remaining on the packing together with the absorbed product.

Determination of the Pyrolysis Product Yield. The yield of the gaseous products is determined from the wet-gas meter reading and gas density. The method for determining the gas density is described in Work 31. The tar yield is defined by weighing after the experiment. The difference between the weight of the stock and that of the liquid and gaseous pyrolysis products is attributed to coke formation and losses in the course of the experiment.

Pyrolysis Tar Distillation and Production of Refined Light Oil. The contents of the receivers *8* and *9* are poured together into a 0.5-litre flask with a dephlegmator and a vertical reflux condenser, then distilled. A sample is taken for determining density. The tar distillate cut at temperatures of up to 170-200°C represents light oil containing aromatic hydrocarbons. The amount of the light oil obtained as a result of tar distillation is determined from the difference in the receiver weights before and after the distillation. The content of aromatics in the light oil is found. Also measured is the density of the distillate and residue.

The tar may also yield refined pyrobenzole (an aromatic fuel). For this purpose, a benzole fraction boiling at 78°C, also known as benzole heads, almost exclusively containing unsaturated hydrocarbons, is precut during the distillation of the pyrolysis tar and charged

into a weighed receiver. The¦ light oil derived during subsequent distillation (crude pyrobenzole fraction), free of benzole heads, contains, in addition to aromatics, unsaturated and saturated hydrocarbons having almost the same boiling point. The tar and light oil are distilled at a rate roughly equal to two drops per second. When the temperature approaches its predetermined limit, the distillation rate goes down.

To rid the light oil of unsaturated hydrocarbons, it is poured into a weighed separating funnel having a capacity of 250 to 500 cm^3 and treated with 92% sulphuric acid which reacts with unsaturated hydrocarbons almost without affecting the aromatic ones. The oil is treated with sulphuric acid in the following manner. If the pyrolysis process is programmed to yield tar with a small amount of unsaturated hydrocarbons, the acid is taken in a quantity constituting 4% of the light oil weight. First, half of the calculated amount of the acid is added to the funnel. The contents of the latter are agitated for 5 minutes by shaking. The gases evolved during agitation are periodically vented through the cock or stopper of the funnel. The reaction is accompanied by heat release, and the contents of the funnel are heated. The necessary temperature is maintained within 45 to 50°C during the process by periodically cooling the funnel with tap water. As a result of formation of products of polymerization of unsaturated hydrocarbons, the water in the funnel turns dark, and a dark layer of acid sludge settles on the funnel bottom. It takes 15 to 20 minutes for the acid sludge to settle completely, after which it is drained off, a second portion of sulphuric acid is added to the funnel, and the contents are stirred again for 5 minutes. The settled acid sludge is let out of the funnel.

In the case of high content of unsaturated hydrocarbons in the pyrolysis products, the light oil is treated with sulphuric acid taken in an amount of 10% (but not more than 20%) of the oil weight. This amount of acid is divided into three portions, and the oil is treated with the acid in three steps. At first, the oil is treated with half the total amount of the acid. After the first portion of acid sludge has settled and drained off the second portion of the acid (one quarter of its total amount) is added, and the oil is treated in the same manner as before. Finally, the funnel receives the last portion of the acid, and final treatment of the oil takes place. After the unsaturated hydrocarbons have been separated completely, the oil is washed and neutralized. To wash and neutralize the light oil, the separating funnel with the purified product is filled with water in an amount equal to that of the oil. The contents of the funnel are agitated for 5 minutes, then the water layer is allowed to settle, decanted from the funnel, and the entire procedure is repeated. After that, the oil is washed with an equal amount of a 2% soda solution, then several times with water till neutral reaction of the

washes. The funnel with the purified oil is weighed, and the differ-ence in weight serves as an indication of the refined product yield and the content of unsaturated hydrocarbons in the initially cut fraction.

The density of the refined oil is determined with the aid of a pycn-ometer.

The efficiency of light oil refinement is checked using the potas-sium permanganate test. The essence of the test is that in the pre-sence of unsaturated hydrocarbons the initially crimson potas-sium permanganate solution turns red then brown due to reduction of $KMnO_4$ in contact with the unsaturated compounds. The rate at which the solution changes colour depends on the amount of unsat-urated compounds in the tested product. If their content is high, the change is fast. On the contrary, if unsaturated compounds are absent or present in small amounts, the initial (crimson) colour persists over a long period of time. For example, the test lasts about 1 min 45 s if the aromatic hydrocarbons are absolutely pure.

To carry out the potassium permanganate test, 2 to 3 cm^3 of the product to be tested are put into a test tube added to which is a double amount of acetone (chemically pure) for dissolution of the hydrocarbons plus a drop of a 1% $KMnO_4$ solution. At the same time, the stopwatch is started and the colour of the solution is observed. The stopwatch is stopped the very instant the solution turns red, and the elapsed time is marked. For more proper marking of the instant at which the colour of the solution changes, a reference solution is prepared for comparison with the solution under test. The reference is usually acetone or distilled water with a drop of the solution in a test tube of the same diameter as the one containing the tested product. The potassium permanganate solution is dropped into both test tubes at a time.

The distillation over, the experimental data are used to draw up the material balance of the pyrolysis and tar distillation pro-cesses as follows:

Supplied for pyrolysis	Quan-tity, g	Obtained as a result of pyrolysis	Quan-tity, g	Product yield, wt. %

(Indicate the starting sub-stance)		Primary pyrolysis products:
		     tar
		     gas
		     coke and losses
		 Tar distillation products:
		     light oil
		         (a) benzole heads
		         (b) pyrobenzole
		     tar residue above 170 °C
		     losses, including polymers
		     in the acid sludge		

Analytical Procedure

The *content of unsaturated hydrocarbons* in the pyrolysis gas is to some extent a characteristic of the process and, in particular, related to the yield of aromatic hydrocarbons. Besides, unsaturated hydrocarbons resulting from pyrolysis serve as stock for many important syntheses. Therefore, their content in gases is always a matter of interest. The content of unsaturated hydrocarbons in the gas is determined with the aid of a saturated aqueous solution of bromine in a device illustrated schematically in Fig. 26.

During the experiment, approximately 0.5-dm^3 gas samples are taken every 15 minutes into a gas holder filled with a saturated sodium chloride solution. To determine unsaturated hydrocarbons, a gas sample (100 cm^3) is transferred from the gas holder into the measuring burette of the device. When a two-pipette apparatus is used, the gas sample is several times transferred into the pipette with bromine water until the gas volume stops to change. The final measurement of the volume of the remaining gas is carried out after the gas has been transferred into the second pipette with an alkaline solution (to absorb bromine vapours).
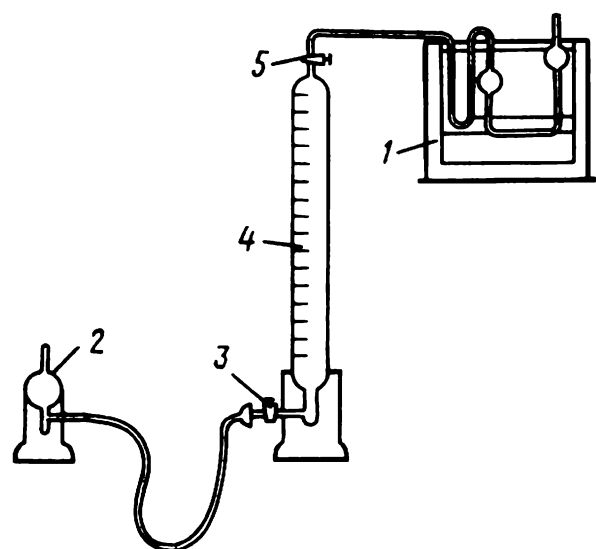
Fig. 26. Device for determination of unsaturated hydrocarbons

When analysis is made using the above-mentioned device (Fig. 26), the absorption solution is poured into the bulb pipette *1* till the lower part (about a third) of the upper bulb is filled. At the same time, the lower bulb and capillary are filled to capacity with the solution. 100 cm^3 of gas are taken into the measuring burette *4* of the device, the burette is connected to the pipette, and the level of the bromine water in the capillary is marked. Then, the gas is transferred from the burette into the pipette via cocks *3* and *5*, the level bottle *2* is raised to a height at which the liquid in the bottle is level with the cock *3*. As soon as the gas from the burette is fully transferred into the pipette, the cocks are closed, and the gas is left in the pipette for 4-5 minutes while the pipette is shaken several times. The cocks are then opened, and the level bottle *2* is lowered for the gas to return into the measuring burette, the bromine water in the pipette being brought to the initial level in the capillary. The volume of the gas remaining in the burette is measured, and the gas is transferred into the other pipette which is similar to the first one but filled with an alkaline solution to

absorb bromine vapours. The gas is transferred back from the second
pipette into the measuring burette, which is followed by final mea-
surement of the remaining gas volume.

The *content of aromatic hydrocarbons* in the starting substance and
light oil is determined by the sulphonation method. It is based on
the capacity of aromatic hydrocarbons to react with concentrated
sulphuric acid (or oleum), as opposed to saturated hydrocarbons
that do not react with the latter. The resulting
sulpho compounds of aromatics are soluble in
sulphuric acid and pass into the acid layer.

The product is sulphonated in a special device
called sulphonator (Fig. 27) which is a graduated
tube with two spherical bulbs. The lower bulb
terminates in a tube with a stopcock. The upper
bulb has a neck closed by a ground-glass stopper.
The vertical tube has a volume of about 12 cm³
and is graduated in 0.1 cm³ from zero at the
bottom to 10 cm³ at the top. The volume of the
lower bulb from the zero level to the cock is
three times greater, that is approximately 30 cm³.
The upper bulb must be big (approximately
100 to 120 cm³) enough to hold the entire contents
and to facilitate shaking of the liquid.

Fig. 27. Sulpho-
nator

97.5-98% sulphuric acid is used for sulphonation. The acid is
introduced into the lower bulb of the device up to the zero mark,
using a dropping funnel with a long tube to avoid splashing of the
acid against the walls of the sulphonator tube. Then, 10 cm³ of
the product to be tested are introduced into the device by means
of another dropping funnel, filling it up to the topmost mark. The
sulphonator is stoppered and turned upside down so that the contents
fill the upper bulb. The liquid is shaken for 10 minutes. The device
is then set upright, and the liquid is allowed to stand for 30 to 60 min-
utes. The extent to which the hydrocarbon layer is reduced is marked.
Usually, this layer rises above the zero mark in the lower part and
goes down below the "10" mark in the upper part. The overall decrease
in the product volume is equivalent to the content of aromatics
in it. After that, the contents of the sulphonator are shaken once
more for 10 minutes and allowed to stand for 30 to 60 minutes.
After both layers have settled, the volume of the hydrocarbon layer
is registered. If the second measurement shows a change in volume
as compared to the first one, the sulphonation is repeated for the
third and, if necessary, fourth and fifth times, in other words, as
many times as may be required for the volume to stop changing
after two consecutive tests. In the last test, the overall reduction in
the product volume is found. The amount of aromatics in the product
is calculated from the final and initial volumes.

LITERATURE

Magaril, R. Z., *The Basic Theory of the Chemical Processes Involved in Oil Refining*, Moscow, 1976.
The Effect of the Stock Composition on the Yield of Main Pyrolysis Products, Kalechits, I. V., Sokova, N. A., Mukhina, T. N. *et al.*, Moscow, 1971.

Instructions to the Laboratory Work "Pyrolysis of Petroleum Products"

1. Test the assembled experimental setup for air-tightness with particular attention to connection of the wet-gas meter.
2. Charge the necessary amount of the starting substance into the measuring burette and switch on the furnace.
3. After the desired temperature has been reached, start the water-jet pump (the water tap must be under the exhaust hood) and feed the starting substance into the pyrolysis furnace.
4. The students working with the experimental setup **must wear goggles**; students not involved in this work are not allowed near the setup.
5. Start and stop the water-jet pump slowly in accordance with the predetermined gas feed rate. Before stopping the pump, close the stopcock of the dropping funnel and remove the hose connecting the water-jet pump with the surge bottle.
6. Take the unused starting substance and other highly inflammable substances away from the experimental setup.
7. Wear goggles while fractionating the tar, the furnace being heated with a burner through an asbestos net or on an oil bath.
8. **Wear rubber gloves when handling sulphuric acid (working with the sulphonator).**

LABORATORY WORK 10. STUDYING THE OXIDATION RATE OF METALS AT ELEVATED TEMPERATURES

The corrosion of metals implies their destruction as a result of chemical or electrochemical interaction with an aggressive medium. A typical example of corrosion is rusting of iron exposed to damp air, that is its oxidation resulting in oxides Fe_2O_3 and Fe_3O_4 or hydroxides $Fe(OH)_3$ and $Fe(OH)_2$. Many metals are also known to corrode rapidly in aggressive media, particularly acids, which dissolve metal oxides and metals. In some cases, the availability of a corrosion-proof material and its rational use are the determining factors in deciding whether a particular product can be manufactured.

A metal or a metal alloy is said to be corrosion-proof if it adequately resists the action of an external aggressive (corrosive) medium, that is if its corrosion rate is low. A measure of corrosion resistance is the rate of corrosion in a given medium under particular conditions. The corrosion rate is often expressed as the weight (in g) of a metal passing into corrosion products per unit time (h) from unit surface (m²) of the metal. The amount of corroded metal can also be expressed as the thickness (mm) of a metal layer transformed to

corrosion products over a definite period of time (a year):

$$\delta = G/1000\ \rho, \tag{1.91}$$

where δ is the thickness of the corroded metal layer, in mm; ρ is the metal density; and G is the weight of the metal corroded over a square meter of its surface per year.

The corrosion products may evolve in solid, liquid, and gaseous states. The solid products (oxides, salts) may form a solid film over
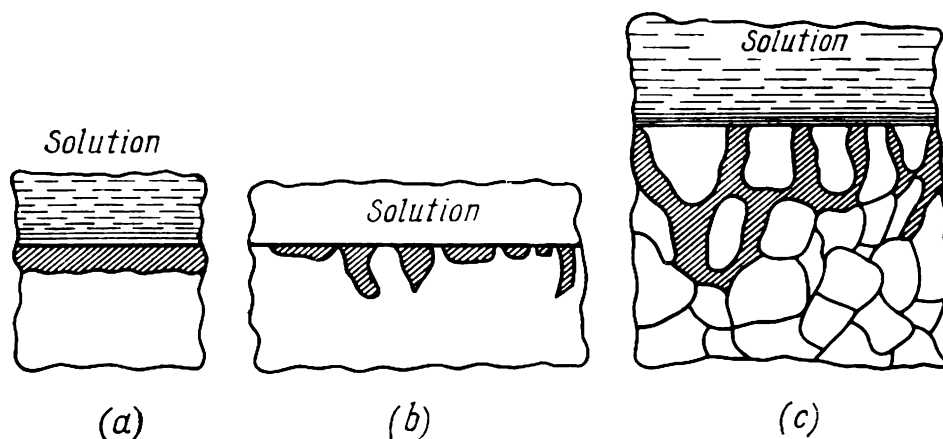
Fig. 28. Types of corrosion according to the amount of metal destruction

the metal surface, thereby protecting the metal against further corrosion. Artificial formation of such protective films is known as passivation and is often used as a method of chemical protection of materials.

Corrosion may be uniform or local, depending on the amount of metal destruction. *Uniform* corrosion implies a relatively even distribution of the corrosive destruction over the entire surface of a metal (Fig. 28a). *Local* (*nonuniform*) corrosion is such when a substantial portion of the metal surface is free of corrosion, the latter being concentrated only on individual areas in the form of points, spots, and pits (Fig. 28b). A particular case of local corrosion is intercrystalline corrosion which is characterized by corrosive attack along the boundaries between large grains (crystallites) of a metal or over the outer layers of individual grains (Fig. 28c) having a composition different from that of the material as a whole. This type of corrosion is especially dangerous because while the mechanical properties deteriorate considerably, the surface often appears to be almost normal. Corrosion cracks occur under the joint action of the corrosive medium and mechanical stresses. They generally result from intercrystalline corrosion.

According to the process itself, the corrosion of metals may be classed into two major categories: chemical and electrochemical corrosion.

Electrochemical corrosion is the result of exposure of metals to electrolyte solutions. The corrosion occurs as a consequence of the thermodynamic instability of metals in the latter. The surface of an attacked metal can be represented as a system of micro- and macrogalvanic couples. Such couples stem from the presence in a metal of impurities of grains of other metals, contamination of the surface with a higher or lower electrode potential, structural inhomogeneity of the metal, inhomogeneous internal stresses in the metal and its deformation, differences in concentration of the electrolyte contacting with different parts of the metal, nonuniform application of the electric field, and other factors. In all these cases, different portions of a metal have different values of the electrode potential. In an electrolyte, portions with a lower electrode potential (more electronegative ones) become anodes, whereas the more electropositive portions become cathodes. Accordingly, distinction must be made between anodic and cathodic corrosion processes. The anodic process consists in the metal ions passing into solution (dissolution of the metal), for example,

$$Me \rightarrow Me^{2+} + 2e \qquad (a)$$

with the electrons remaining on the metal surface. The cathode is where the cations present in the solution, such as hydrogen ions, discharge:

$$2H^+ + 2e \rightarrow H_2 \qquad (b)$$

or where the oxidizing agents, such as oxygen, are reduced into hydroxy ions:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad (c)$$
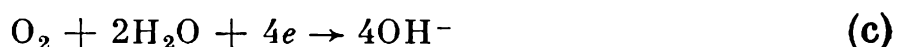
Reaction (b) is observed in acid solutions, while reaction (c) occurs in neutral and alkaline solutions. A flow of electrons from the anode to the cathode, known as corrosion current, is initiated inside the metal.

Chemical corrosion is a process in which a metal combines directly with the corrosive components of the medium. It is normally a redox process with the corrosive component being the oxidizing agent. The corrosion products may be oxides (Me_mO_n) or organometallic compounds. A typical example of chemical corrosion is that of metals caused by gases at elevated temperatures, for instance, oxidation with oxygen, forming an oxide film (layer). Chemical corrosion is observed in liquids other than electrolytes, such as absolute alcohols, benzene, petrol, kerosene, and so on. From the standpoint of the destruction pattern, the chemical corrosion of a sufficiently homogeneous metal belongs to the uniform type. In a gaseous medium, corrosion products tend to accrete in layers on the metal surface.

The chemical corrosion process is governed by the regularities of heterogeneous processes, that is the corrosion rate is given by the

formula

$$-dG_m/d\tau = k_m F \Delta C \qquad (1.92)$$

or

$$dG_c/d\tau = k_c F \Delta C, \qquad (1.93)$$

where G_m and G_c stand for the amount of corroded metal or corrosion product, respectively, in g, G_m being the loss in metal weight and G_c being the gain in metal weight owing to corrosion products; τ is the corrosion time, in h; k_m and k_c are the respective corrosion rate constants (in determining k_m and k_c one must take into account the amount (g/m^2) of the metal destroyed within an hour per unit concentration of the corrosive component in the medium, in g/m^3, the resulting dimensions being g/m$^2\cdot$h$\cdot$g/m^3 or m/h); F is the area of contact between the metal and corrosive medium, in m^2; and ΔC is the driving force of corrosion, expressed in grammes of the corrosive component per cubic metre of the medium (gas, liquid) at the interface with the metal.

Assuming that the driving force ΔC of corrosion is constant or in determining its mean value over the corrosion time τ,

$$\Delta C_{mean} = G_c/k_c F \tau. \qquad (1.94)$$

The rate of uniform corrosion with formation of a film (layer) of corrosion products on the metal surface can be calculated using the formula

$$d\delta/d\tau = k_\delta \Delta C, \qquad (1.95)$$

where δ is the thickness of the corrosion product layer, in mm, and k_δ is the process rate constant, in mm/h$\cdot$g$\cdot$m^{-3}. In the case of gas-phase corrosion, ΔC may be expressed in fractions of a megapascal; then k_δ will be expressed in terms of mm/(h$\cdot$MPa).

The reactors and metal structures involved in industrial chemical processes are often subject to oxidation at high temperatures, the rate of this process obeying the laws of macrokinetics of heterogeneous processes. The high-temperature oxidation of metals is a good example of gas-phase corrosion in view of the fact that vapour condensation is ruled out. The oxidation conditions and composition of the corrosion products on the metal surface may vary widely. At normal temperature, the oxidation of metals is, in most cases, restricted to tarnishing or formation of thin films. The thickness of these films does not increase at low temperatures because of the insignificant diffusion of oxygen toward the metal surface.

Gas-phase attack penetrates into the metal almost evenly over the entire surface with formation of corrosion product films having the same thickness over the entire area subject to corrosion. The rate of gas-phase corrosion is often assessed from the gain (or loss) in weight over a square metre of the surface per unit time (hour, day,

etc.). Sometimes the gas-phase corrosion rate is determined from the volume of the gases evolving per unit time, as well as from the corrosion depth and other factors.

The corrosion rate increases with temperature because of the increasing rate of diffusion and chemical processes; as a result, the corrosion product films gradually become thicker. The increase in film thickness on different metals is in compliance with different laws: rectilinear, parabolic, and logarithmic. This depends, primarily, on the nature of the forming oxides and film continuity. In the case of metals whose oxidation is without formation of protective films, the oxide film growth rate will remain constant. The rate of uniform corrosion with formation of a non-protective (e.g. discontinuous) porous oxide film on the metal surface can be calculated from Eq. (1.95). The film thickness δ is calculated as follows:
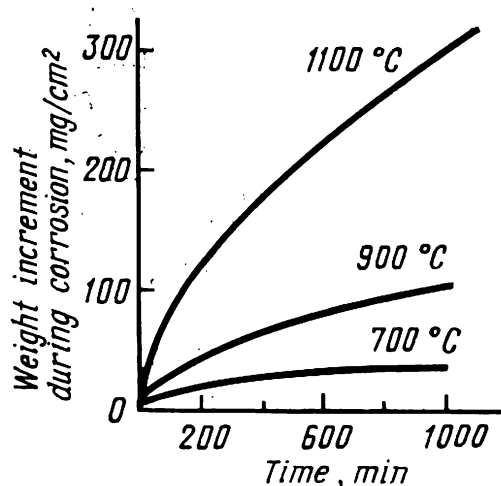
Fig. 29. Parabolic curves of iron (II) oxidation at high temperatures

$$\delta = k\tau + A, \qquad (1.96)$$

where A is the integration constant. Hence, the film thickness (or amount of chemical corrosion) is proportional to the oxidation time. The integration constant determines the film thickness at the initial moment of oxidation ($\tau = 0$). If it is assumed that the oxidation begins on a clean surface, the constant A in Eq. (1.96) may be omitted.

In the case of alkali and alkaline-earth metals whose oxidation results in formation of a porous loose oxide film, the film growth is linear in time at various temperatures.

Most metals used in engineering oxidize in accordance with the parabolic law (Fig. 29). In this case, as a result of uniform oxidation of the surface, the corrosion process is slowed down by the diffusion of the reagents through the film, and as the film becomes thicker, its further growth slows down.

Thus, the rate of the heterogeneous process of chemical corrosion can be expressed in terms of Eq. (1.93). In accordance with the diffusion law, Eq. (1.93) can be reduced to

$$dG/d\tau = DFdC/d\delta, \qquad (1.97)$$

where G is the amount of the diffusing substance, in g; τ is the diffusion time, in s; D is the diffusion rate coefficient, in cm²/s, $dC/d\delta$ is the concentration gradient, in g/cm³·cm; and F is the oxidized area, in cm².

If it is assumed that steady-state diffusion is achieved in the course of oxidation, that is no accumulation of the diffusing substance takes place at any point across the film, the derivative $dC/d\delta$ can be substituted by the ratio $(C_0 - C_1)/\delta$, where C_0 is the oxygen concentration on the outer surface of the film, where it forms the boundary with air, and C_1 is the oxygen concentration on the inner film surface where it forms the boundary with the metal. Then, the diffusion rate per unit cross-sectional area

$$u_d = \frac{dG}{d\tau} = D \, \frac{C_0 - C_1}{\delta} \tag{1.98}$$

is directly proportional to the difference in oxygen concentration and inversely proportional to the film thickness (Fig. 30).

If the metal is already covered with a protective film, it may be assumed that the oxidation proceeds in the diffusion region and that
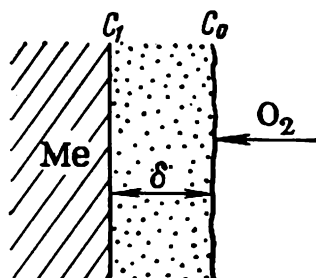
Fig. 30. Film diffusion of oxygen in metal oxidation

the oxygen penetrating through the film immediately⸌enters into the reaction in its entirety without being accumulated. Then, assuming that the film growth rate (u_c) is equal to the oxygen diffusion rate (u_d), we have

$$u_c = u_d = DC_0/\delta, \tag{1.99}$$

that is the oxidation rate is directly proportional to the reagent (oxygen) concentration and inversely proportional to the film thickness. At constant temperature and oxygen concentration, for example, at exposure to air heated to a certain temperature,

$$u_c = d\delta/d\tau = k_d/\delta, \tag{1.100}$$

or, after integration,

$$\delta^2 = k_d \tau + A, \tag{1.101}$$

where k_d is a constant determined by the diffusion coefficient and oxygen concentration and A is the integration constant.

Hence, under constant oxidation conditions (for a given metal and a given partial oxygen pressure), k_d is dependent only on temperature. Sometimes the film thickness increases at a slower rate

that would be expected assuming a simple diffusion mechanism of oxidation slow-down, leading to a parabolic relation. In some cases, for example, when cracks are present in scale, which may happen as a result of heating or cooling and at relatively low temperatures, the oxidation of metals obeys the logarithmic law:

$$d\delta/d\tau = k/e^\delta \qquad (1.102)$$

or

$$\delta = \ln (k\tau). \qquad (1.103)$$

Fig. 31 represents logarithmic curves of iron oxidation at 300 and 250°C. At relatively low temperatures, the logarithmic relation
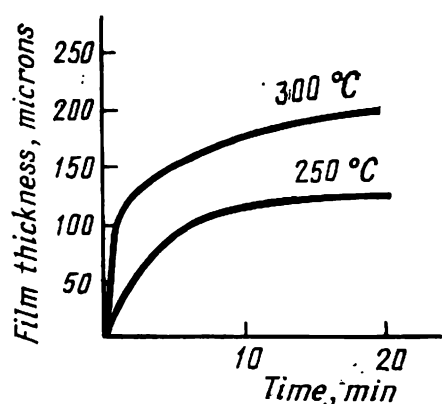
Fig. 31. Logarithmic curves of iron (II) oxidation
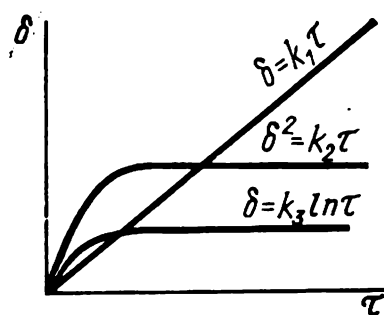
Fig. 32. Basic types of metal oxidation curves

is typical of most metals. Fig. 32 shows common types of oxidation curves. As can be inferred from Figs. 31 and 32, the oxidation rate increases with temperature. This happens because increasing with temperature are the oxygen diffusion rate and the oxidation rate constant in accordance with the Arrhenius equation

$$\ln k = A - E/RT, \qquad (1.104)$$

which suggests that the rate of chemical corrosion (including gas-phase corrosion) varies directly with temperature.

The purpose of this work is to study the kinetics of gas-phase corrosion and the oxidation pattern of various metals as a function of temperature.

Experimental Setup and Procedure

The kinetics of gas-phase corrosion is studied using methods of periodic weighing on a setup shown schematically in Fig. 33. A test specimen *3* is suspended from the left end of the beam *8* of the analytical balance *9* by a nichrome wire *6* made up of several links inside a vertical tube furnace *4*. The weight of the wire and specimen is balanced out by a counterweight on the right pan *10* of the balance

9. The temperature in the furnace is measured by a thermocouple *2* with a galvanometer *1* or controlled with the aid of an automatic thermostatic switch. The end of the thermocouple must be near the test specimen.

To avoid heating of the analytical balance, an insulating asbestos screen *7* is installed between the furnace and the balance. Used in the experiment are specimens of standard sizes (10 × 15 × 1 or 10 × 15 × 2 mm), which are specially prepared (their surface is cleaned with emery paper and degreased by washing in petrol or alcohol). Then, the specimen surface is measured by means of a micrometer, the specimen is dried for 3 to 5 minutes at 100°C, cooled, and weighed on the analytical balance to within 0.0001 g.

The metal oxidation rate is determined as follows: the furnace is switched on together with the air blower (not shown) supplying air into the furnace with the air flow rate being adjusted with the aid of a rheometer *13*. Upon reaching the desired temperature (if no automatic thermostatic switch is available, it is controlled by the rheostat of the furnace), the specimen is suspended in the furnace and

Fig. 33. Experimental setup for studying the gas-phase corrosion rate at high temperatures:

1—galvanometer; *2*—thermocouple; *3*—test specimen; *4*—vertical tube furnace; *5*—seal; *6*—nichrome wire; *7*—asbestos screen; *8*—beam; *9*—analytical balance; *10*—pan; *11, 13*—rheometer; *12*—mixer; *14*—SO₂ bottle; *15*—aspirator

weighed after one or two minutes. At this point in time, the specimen is heated to the furnace temperature but has not yet been perceptibly oxidized. Then, the specimen is weighed over and over again for one or two hours at regular time intervals (15 to 20 minutes). As the metal is being oxidized, its weight gradually increases, which is determined by periodic weighing. At the end of the experiment at a particular temperature, the specimen is removed, the next experimental temperature is attained in the furnace, a new specimen of the same metal is suspended in the latter, and the experiment is repeated in the same sequence.

The same setup can be used to study the rate of gas-phase corrosion in any corrosive medium, such as a mixture of air (or nitrogen) with sulphur dioxide. To this end, fed into the furnace instead of air is a gaseous mixture obtained by mixing air and sulphur dioxide, taken

from a bottle *14*, in the mixer *12*. The mixture is prepared with any ratio of its components, achieved by means of rheometers *11* and *13*. Its analysis for SO_2 content is carried out with the aid of an aspirator *15* by methods described in Works 5 and 13. The gas from the furnace is drawn under the exhaust hood or vented into the atmosphere. The wire by which the specimen is suspended is let through a sealing device (e.g. mercury cutoff) *5* secured in the plug closing the outlet opening of the furnace tube.

Data Processing and Calculation Techniques. The results of experiments into the kinetics of gas-phase corrosion by the periodic weighing method are recommended to be tabulated as follows:

Temperature, °C	Metal and specimen number	Specimen surface area S, m²	Weighing time and number	Elapsed time τ, min	Specimen weight G_1, g	Weight increment ΔG_1, g	Increment per unit ΔG_1, g

G_1-τ, ΔG_1^2-τ, and ΔG_1-log τ curves are plotted for each temperature from the tabulated data to establish the oxidation pattern in a given temperature range. If the G_1-τ curve is a linear relation, then Eq. (1.97) is assumed to hold in this case.

In the case of a parabolic ΔG_1^2-τ curve, the oxidation of the metal can be described in terms of Eq. (1.101). And, finally, if the ΔG_1-log τ plot is a straight line, the oxidation obeys the logarithmic law and can be described by Eq. (1.103).

Having established the curve type and the corresponding equation, one can calculate the metal oxidation rate constant at any temperature, then the oxidation activation energy E and the constant A in Eq. (1.104), thereby deriving an equation of the oxidation process as a function of temperature. To determine the oxidation rate constant, the calculation is based on the following formulas: $k = \Delta G_1^2/\tau$ in the case of a linear relation, $k = \Delta G_1^2/\tau$ in the case of a parabolic relation, and $k = \Delta G_1/\log \tau$ in the case of a logarithmic relation.

The values of E and A are determined by deriving, from Eq. (1.104), two equations with two unknowns, in which the oxidation rate constants obtained at temperatures t_1 and t_2 are denoted by k_1 and k_2, respectively:

$$\ln k_1 = \ln A - E/RT_1; \quad \ln k_2 = \ln A - E/RT_2,$$

where $T_1 = t_1 + 273$ and $T_2 = t_2 + 273$.

The values of E can also be determined using the Arrhenius equation in a modified form:

$$\ln k_1 - \ln k_2 = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1.105}$$

or

$$E = \frac{2.3R \, (\log k_1 - \log k_2)}{1/T_2 - 1/T_1} .$$ (1.106)

Since $1/T$ is a small quantity, it is convenient to multiply the numerator and denominator by 10^3, and substitution of the value of R will give

$$E = \frac{(\log k_1 - \log k_2) \, 19.1 \cdot 1000}{1000/T_2 - 1000/T_1} .$$ (1.107)

After E has been determined, the constant A is found from the equation

$$\ln A = \ln k + E/RT.$$

The found values of E and A are substituted into the equation representing the temperature dependence of the metal oxidation rate. For convenience in calculations, it is recommended to summarize the results in the following table:

Temperature, °C	Temperature, K	$\dfrac{1000}{T}$	Time, h	Weight increment ΔG_1, g/m²	ΔG_1^2	Oxidation rate constant k^*, g/m²·h	Activation energy E, J/mole

* The dimension of k is similar to that of the gas-phase corrosion rate defined from the weight increment per square metre of the surface area per unit time.

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**Instructions to the Laboratory Work "Studying
the Oxidation Rate of Metals at Elevated Temperatures"**

1. Prepare metal specimens, clean and degrease their surface, and measure the surface area.

2. Switch on the airblower and start feeding air into the furnace after having adjusted its flow rate by means of a rheometer. In studying SO_2 corrosion, prepare a gas mixture of a prescribed composition and feed it into surface.

3. Switch on the furnace and heat it to the desired temperature, the latter being controlled by an automatic thermostatic switch or a rheostat.

4. Suspend a specimen in the furnace and weigh it periodically at present time intervals.

5. When passing the SO_2-containing gas through the furnace, make sure that the experimental setup is completely airtight, open the SO_2 bottle only in the presence of the instructor or laboratory assistant, and take all the necessary precautions when handling the bottles, the exhaust gas being drawn under the exhaust hood.

6. After the specimen has been weighed at a given temperature, remove it from the furnace, heat the latter to the next experimental temperature, and repeat the experiment in the same sequence.

7. After the experiment, switch off the furnace and air blower.

LABORATORY WORK 11. MANUFACTURE AND TESTING OF PLASTICS

Plastics include a broad range of materials whose basic component is resins—solid high-molecular compounds capable of passing into a plastic state at high temperature and pressure, being moulded under the action of externally applied forces, and stably retaining, after solidification, the imparted shape when in use.

Resins constitute the most important component binding all other components of the future plastic into a coherent mass and imparting to the mix (composition) plasticity, mouldability, as well as insulating, anticorrosive and other essential properties. These are attained by using, in addition to resins, such components as cellulose esters, proteins, asphalts, pitches, and drying oils.

According to composition, plastics are divided into *unfilled* ones consisting only of resin, also known as cast resins (this group also includes films), and *filled* plastics-blends containing fillers, plasticizers, dyes, stabilizers, curing agents, and other additives evenly distributed in the resin binder.

Fillers—solids introduced to impart or enhance particular properties of a plastic, such as strength, heat resistance, and resistance to shrinkage during moulding. At the same time, the filler improves the appearance and dielectric properties of the plastic. Used as fillers are both organic and mineral compounds. These may be in the form of *powders* (wood flour, ground mica and quartz, carbon black, graphite, barium sulphate, diatomaceous earth, kaolin, talc), *fibres* (cotton, asbestos, combings, fibreglass), and *sheets* (paper, cotton and glass fabrics, mica, veneer).

Plasticizers—low-volatility, mostly liquid substances enhancing the plasticity and elasticity of a composition and improving the performance characteristics of plastic products. The most widely used plasticizers include camphor, castor oil, dibutyl phthalate, tricresyl phosphate, oleic acid, and other more or less readily available chemicals.

Solvents—alcohol, benzene, and acetone introduced into the composition to facilitate its blending. During drying, solvents normally evaporate and, as a rule, are absent in the finished product.

Colourants are used to impart the desired colour. They must not only be fully compatible with the plastic but also withstand changes in temperatures, be resistant to water, and, consequently, retain their colour not only during moulding but also in product use. Colourants include, for example, nigrosine, methylene green, and others.

Curing agents, such as hexamethylene tetramine (urotropin) cause some plastics to pass into a nonmelting irreversibly solid state. Plastics often contain small amounts of some other additives as well: stabilizers enabling plastics to retain their original properties over a long period of time, lubricants facilitating moulding, blowing agents used in the manufacture of foam and cellular plastics, luminous compounds, fungicides used to protect plastics against the destructive action of mould, and so on.

Our industry produces scores of grades of various plastics based on resins of a particular class (polymerization resins, polycondensation resins, cellulose esters, etc.) and blends, that is plastics containing resins of different classes, which permits manufacturing materials with a greater diversity of properties.

The most widely employed polymerization resins include polyethylene, polypropylene, polymers and copolymers of vinyl chloride, polymers of fluoroderivatives of ethylene, polyacrylates, polyvinyl acetate, polyformaldehyde, and some others.

Polyethylene $(-CH_2-CH_2-)_n$ is produced from ethylene by polymerization under a pressure of 1500 to 2000 MPa at 180 to 200°C with small amounts (0.005-0.05%) of oxygen being used as the initiator, or polymerization at atmospheric or low pressure ($2 \cdot 10^{-1}$ to $6 \cdot 10^{-1}$ MPa) and a low temperature (60 to 70°C) in the presence of complex organometallic catalysts. Polyethylene is a solid material, white when thick, colourless and transparent when thin. It is produced in the form of films of various thicknesses, tapes, sheets, blocks, tubes, rods, and so on. This plastic retains its shape up to 80-120°C (depending on the grade) and is characterized by high frost resistance (it loses elasticity only at temperatures below —60°C), outstanding dielectric properties, and resistance to water, gases, acids, alkalis, salts, oils, and some solvents. Polyethylene has a low density (0.92-0.93), is weak-resistant and easy to machine, bond, and weld. It goes into the manufacture of various moulded and cast products.

Polypropylene $\left(-CH_2-\underset{\underset{CH_3}{|}}{CH}-\right)_n$ has a higher melting point than polyethylene and is more rigid, stronger, and oxidation-resistant.

Polyvinyl chloride resin $(-CH_2-CHCl-)_n$ forms the basis of various plastics.

Rigid vinyl plastic, or *PVC*, is a solid opaque material, normally dark brown, and obtained by thermomechanical plasticization of

polyvinyl chloride. PVC exhibits a good combination of such properties as resistance to many acids, alkalis, salt solutions, and most organic solvents with excellent physicomechanical and dielectric characteristics. It is readily machinable, mouldable, weldable, and bondable. These properties make it possible to widely use PVC also as a structural material in its own right. PVC goes into the manufacture of plates, films, tubes, rods, reactors, tubs, and liners for various vessels and tanks.

Screw extrusion or rolling and calendering of a polyvinyl chloride mixture with a plasticizer (phthalate or phosphate) produces *flexible PVC* used in the lining of various apparatus, manufacture of linoleum, imitation leather, gaskets, and the like. Electrical insulation from polyvinyl chloride is resistant to most corrosive media, solvents, and greases.

Disadvantages of plastics based on polyvinyl chloride resin include low heat resistance (about 60-70°C) and brittleness at low temperatures (—10°C and below).

Fluoroplastics result from water-suspension polymerization of ethylene derivatives in which the hydrogen atoms are substituted by fluorine. Polytetrafluoroethylene $(-CF_2-CF_2)_n$ is produced from tetrafluoroethylene, as the name implies, and polytrifluorochloroethylene $(-CF_2-CFCl-)_n$ is produced from trifluorochloroethylene. Their outstanding resistance to various corrosive media makes them superior over all other known materials, polytetrafluoroethylene even surpassing gold and platinum. These plastics are used in the manufacture of films, sheets, plates, tubes, rods, electrical insulation, gaskets, components of valves, pumps, measuring instruments, and other parts of apparatus exposed in their operation to high temperatures, corrosive media, and other adverse environments. For example, products made of polytetrafluoroethylene can work for a long period of time at temperatures ranging from —190 to +260°C and even up to 300 and 400°C for short periods, which has helped to solve a number of difficult engineering problems.

The most commonly used plastics based on polycondensation resins include phenolic plastics (based on phenol-formaldehyde resins), aminoplasts (amine-formaldehyde resins), polyester, epoxy, organosilicon and other plastics. Some of them are thermoplastic but the majority are thermoreactive.

Phenol-formaldehyde resins are used in different forms: (a) without fillers, also known as cast resites, (b) moulding materials (with powdered or fibrous fillers); (c) binders for laminates; (d) adhesives and varnishes for coating metals and wood; and (e) in the manufacture of cellular plastics.

Of particular importance are moulding matericls. They are produced in a dry (rolling or screw extrusion) or wet process. In the latter case, a water suspension of the resin is carefully blended with other

components, followed by drying of the entire stock, or impregnation is carried out with an alcohol solution of resol.

Impregnation of long-fibre materials with resin, followed by moulding, yields products of increased strength.

Aminoplasts are made from polycondensation products of carbamide and its derivatives: thiourea, dicyandiamide, melamine, or their mixtures with formaldehyde. Such carbamide resins are thermoreactive and pass into a solid, nonmelting and insoluble state when heated. As compared to phenolic plastics, they are less heat- and water-resistant but have the advantage of being more light-resistant, colourless, and easier to paint. Broad application has been found by varnishes, enamels, and adhesives based on amine-formaldehyde resins, as well as plastic foams (mipor) for thermal and acoustic insulation.

Industrial *moulding powders* are in most cases produced in water-suspension or dry (rolling and screw extrusion) processes. A typical formulation of moulding powder based on a water-suspension resin (resol) is as follows (in parts by weight):

Water-suspension resin (in terms of dry mass)	50
Curing agent (hexamethylene tetramine)	1-2.5
Lubricant (oleic acid)	1.4-2
Filler (wood flour, in terms of dry mass)	41-44
Colourant (mummy)	4.2-4.4

The water suspension of the resin is produced directly in a condensation reaction of phenol with formaldehyde (see Work 18), that is the water layer is not separated. To produce the moulding powder, the mixer is first loaded with the water suspension then all other components of the plastic, except for the filler. After the ingredients have been properly mixed, the filler is added, and the mixing continues till it is completely impregnated. The resulting mass is dried at a temperature not higher than 90°C. The moisture content in the plastic after drying must not exceed 5%.

The dry process of producing moulding powders is based on impregnation of the filler with softened or molten resin. In an industrial process, the resin is softened during rolling of the plastic stock or with the aid of the screw.

Novolac is first ground to particles 2 mm in size, then mixed with the other components in a ball mill. The powder-like mixture is poured on the rolls heated to 90-100°C. The layer forming on the rolls must be about 3 mm thick. The mixing rolls most commonly used in the manufacture of plastics and rubber compounds consist of two horizontal pieces. The diameters and peripheral speeds of the rolls are different (a friction of 1.4 to 1.8). The rolls are made hollow for easier heating or cooling. The rolling process ends as soon as the emerging sheet becomes uniform; it is then cooled, ground, and sieved.

Plastics are processed by a wide variety of techniques. The basic factors involved in the moulding process are temperature, time, and pressure, the latter not only speeding up the process by compacting the heated stock but also allowing the moulding temperature to be reduced.

The hot moulding process comprises the following steps: (1) stock preparation; (2) metering and loading of the powder into the mould internally shaped and sized as the desired product; (3) moulding proper, including heating of the material, shaping of the product, and holding it in the mould under the pressure applied by the press through a male die with heating or cooling till the product is cured; and (4) extraction of the finished product and preparation of the mould for the next run.
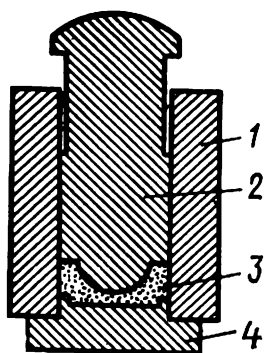
Products are moulded from powders on hydraulic presses in moulds, on tableting and injection moulding machines. Under actual production conditions, most moulding machines are provided with automatic devices for splitting the mold, loading the moulding powder, and ejection of the product. The basic characteristics of a moulding machine include the press capacity, size of the press plates (plunger diameter), and the stroke.

Fig. 34. Mould

Moulding powder is poured into a mould secured on a plate or into a loose mould (for single irregularly shaped articles). The mould is made up of several metal split-cavity blocks having moulding surfaces of the same shape as the article. When assembled, the mould forms an internal cavity filled with the moulding powder.

A mould consists of the following main parts: female die *1*, male die *2*, and mould plate *4* (Fig. 34). The material *3* is poured into the mould cavity, then compressed and heated. Under the effect of heating and pressure, the moulding powder first passes into a plastic state, fills the mould cavity, and solidifies. After holding the plastic for a certain period of time depending on the powder composition, the mould is split. When the moulded articles are ejected from the mould, they are still hot. To remove the gases released by the moulding powder, the breathing step is included, which resides in that after the initial pressure has been built up, the press is switched over to lower pressure, and the male die is partially withdrawn. In the meantime, the released gases are vented outside. Then, the pressure is increased again and maintained at the predetermined level for a definite period of time. Usually, one minute is required per millimeter of the article thickness. The moulding pressure ranges from 7.5 to 20.0 MPa. Since the moulding surfaces of the dies are thoroughly machined, the plastic products have a smooth bright surface that requires no additional machining.

Laminates are materials whose fillers—cotton and glass fabrics, paper, asbestos, veneer—have a pronounced laminated structure. They are produced by compression of a stack of fabric, paper or veneer sheets impregnated with synthetic resins. The binders used in laminates include resol phenol-formaldehyde resins, modified phenol-formaldehyde resins, urea formaldehyde, organosilicon, polyester and some other resins. Some of these materials have been named according to the filler used.

Laminates	Fillers
Fabric-based laminate (Textolite)	Cotton fabrics
Asbestos sheet millboard (Asbolite)	Asbestos board
Synthetic-resin bonded paper laminate (Getinaks)	Paper
Asbestos-cloth laminate (Asbotextolite)	Asbestos cloths
Glass-cloth-base laminate	Glass cloths
Wood laminate	Veneer

Laminates serve as the material for fabricated products such as pipes, rods, plates, sheets, and various shaped components.

A highly efficient technique of plastic manufacture is injection moulding in moulding machines. Thermoplastic pellets are fed from a hopper into the heated barrel, heated to a viscous-flowstate, and forced by a ram from the preheating section through a nozzle into a cold closed mould in which the plastic rapidly cools. The article emerging continuously from the nozzle is hot and is cooled by air or water.

Blow moulding is performed in a mould in which a sheet of celluloid, polystyrene, acrylic plastic, or some other material, preheated to the plastic state, is forced by compressed air against the mould walls and assumes its shape. Some products are made of sheet materials by stamping, bonding, welding, and other techniques adopted by the plastic processing industry. The selection of a particular technique depends on the starting material type (thermoreactive or thermoplastic), shape of the products, and other factors. After moulding, casting, and shaping, articles must be machined to get rid of sprues, flashes, and so on.

This work boils down to producing an article from moulding powder and testing it.

Experimental Setup and Procedure

"Wet" Method of Producing Moulding Powder from Novolac. Ground novolac is dissolved in an alcohol-benzene mixture (85% of alcohol and 15% of benzene) to obtain 50% varnish. Then, a curing agent—hexamethylene tetramine (urotropin), taken in an amount of 14 to 16% of the resin weight, is dissolved in the varnish, and a plasticizer (2.5% of oleic acid) together with a colourant are added. The

resulting varnish is used to impregnate a filler (wood flour, asbestos, kaolin), taken in an amount of 40 to 50% of the resin weight, by thorough stirring in a porcelain cup for 30 minutes. The mixture is dried in a thermostat at a temperature not higher than 60-70 °C. The end of drying is determined by solidification of a sample cooled in air. A cooled lump of the plastic is tested for adhesion by kneading. If the plastic is solid after cooling, the drying may be stopped. The obtained plastic is ground in a porcelain mortar, sieved (the mesh size is specified in the assignment), and the article is moulded from the resulting moulding powder.

"Dry" Method of Producing Moulding Powder from Novolac. 20 g of novolac are ground in a mortar and melted in a porcelain cup on
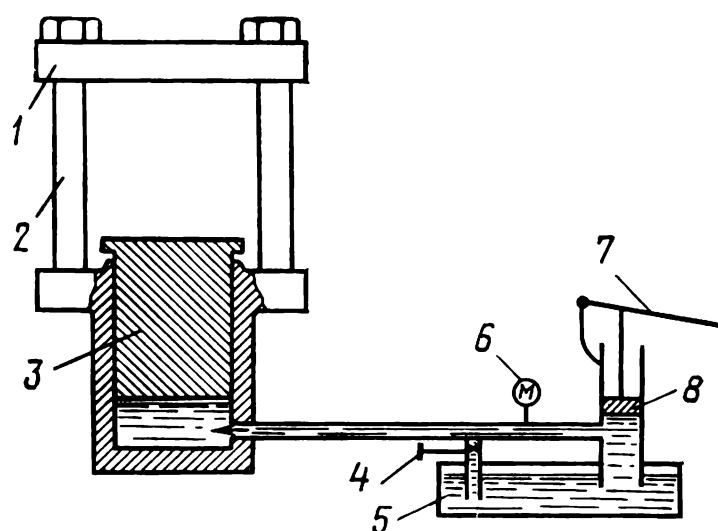
Fig. 35. Hydraulic (oil) 0.8 t press

1—stationary plate; *2*—press frame; *3*—ram; *4*—oil drain cock; *5*—oil unit; *6*—pressure gauge; *7*—lever; *8*—positive displacement pump

a water bath. 3 g of urotropin, two or three drops of oleic acid, and 0.06 to 0.02 g of a colourant are added to the melt at a temperature not exceeding 80°C with stirring by a glass rod. After the mixture has been thoroughly stirred and the urotropin crystals have melted, 10 g of wood flour or sawdust are added to the resin on the same water bath. The entire mass is stirred with heating up to 70 to 80°C for at least an hour till the filler is properly impregnated with the resin. The plastic is cooled and ground in a mortar. The powder is sieved, the mesh sizes ranging from 10 to 30.

Moulding of the Plastic Article. 1 g of the moulding powder is charged into a mould preheated to 75-80°C. The mould is lubricated in advance with oleic acid. It is heated in a thermostat. Immediately after the mould has been filled, it is put on the ram *3* (Fig. 35) of the press, the oil drain hole is closed by a cock *4*, and a pressure of 2.0 to 2.5 MPa is applied on the ram with the aid of a lever *7* for preliminary breathing. After the breathing is over, the mould is removed

from the press and placed in the thermostat with the ram withdrawn, in which the mould is heated to 140-180°C, and the final moulding is carried out. The moulding pressure is 10.0 MPa. The gauge pressure is calculated as follows:

$$P_g = P_m S_1/S_2 = P_m d^2/D^2, \tag{1.108}$$

where P_g is the gauge pressure, in MPa; P_m is the moulding pressure, in MPa; d is the male die diameter, in cm; and D is the press ram diameter ($D = 5.8$ cm).

The moulding powder (1g) is held under pressure for 1.5 minutes. Then, the pressure is relieved by opening the cock *4* of the oil drain hole, and the mould is removed from the press. After the mould plate has been drawn out, the female die is placed on the metal cavity of the mould, and the head of the male die is pressed to eject the moulded plate (cap). If the latter cannot be ejected manually, this is done on the press. The article must be hot when ejected from the mould. After the moulding process is over, all parts of the mould must be cleaned with a rag soaked in acetone or xylene, then wiped dry. The article must have a uniform colour, a smooth surface, and a regular shape.

To produce a specimen of fabric-based laminate, pieces of cloth 40 × 40 mm in size are impregnated with the 50% varnish prepared as described above from novolac plus urotropin and oleic acid. The impregnation is carried out in a glass or porcelain cup for 1.5 to 2 hours. Then, the impregnated cloth pieces are withdrawn from the cup by means of forceps and dried on a clean tin pan. The drying must be carried out at a temperature not exceeding 60-80°C till the solvent evaporates completely, by inserting the pan into a drying oven.

After drying, the cloth pieces are carefully stacked on the press plate, covered by another plate, and the whole is put on the ram of the press. The plates must first be lubricated with petroleum jelly or oleic acid. The ram pressure is $P = 7.5$ MPa, the dwell time being 1 minute per millimetre of the article thickness (the number of cloth layers in the stack and the dwell time are specified in the assignment). After pressing, the plates must be placed in a thermostat without separation and heated to 150°C. The fabric-based laminate specimen is hot when extracted, then cooled, and tested, after visual inspection, for mechanical strength or moisture resistance if the instructor tells so.

Testing of Plastics. State Standards GOST stipulate that plastics must be subjected to physicochemical, mechanical and electric tests. Some of these tests can be carried out as follows with a good degree of accuracy.

To determine the *water absorption capacity* a phenolic plastic specimen is dried in a thermostat at 105 ± 3°C for an hour. After

drying, the specimen is placed in an exiccator with $CaCl_2$, then weighed to within 0.001 g. This is followed by total immersion of the specimen into a vessel with distilled water (the specimen must not touch the vessel walls), in which it is held for 24 hours at 18 to 22°C. After the specimen has been extracted from the vessel, it is wiped with filter paper and not later than after one minute it must be weighed with the same accuracy. The water absorption capacity (%) is calculated using the formula

$$W = [(G_1 - G)/G]\ 100, \qquad (1.109)$$

where G is the weight of the dried specimen before its immersion into water and G_1 is its weight after it has been taken out from water.

The *heat resistance* is determined in the Martens test which is based on establishing the temperature at which the specimen acted upon by a constant bending moment undergoes a certain degree of deformation.

The *high-temperature resistance* is determined by the length of the burnt portion of a test specimen and its weight loss as a result of contact with a Silit rod heated to 950°C in the Schramm apparatus. The high-temperature resistance of a plastic is defined as the product of the specimen weight loss, in milligrammes, by the length of its burnt portion, in centimeters. There is a convention to distinguish six degrees of high-temperature resistance, represented by the following numbers:

High-temperature resistance, mg·cm	$> 10^5$	10^5–10^4	10^4–10^3	10^3–10^2	10^2–10^1	< 10
High-temperature resistance number	0	1	2	3	4	5

The test report must include the characteristics and quality of the starting materials, calculations of pressure and moulding conditions, appearance of the finished article, and test results.

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Instructions to the Laboratory Work "Manufacture and Testing of Plastics"

1. Dissolve the resin in alcohol, benzene, and other solvents under an exhaust hood or in a flask with a reflux condenser.

2. Melt the resin only under an exhaust hood, on a water or sand bath.

3. Before moulding, make sure that the press is filled with oil, wipe the mould clean with a rag and lubricate it with petroleum jelly or another lubricant.

4. After the experiment, clean and lubricate the mould.

5. Do not leave the press under pressure for a long period of time.

6. Hand the unused articles and materials over to the instructor or laboratory assistant.

Chapter 2

Catalytic Processes

Catalytic processes are widely used in the chemical industry. By catalysis is meant augmentation of the rate of chemical reactions or their initiation by substances known as catalysts participating in the process without undergoing chemical changes. Catalysts are not stoichiometrically related with the reacting substances. The accelerating action of catalysts resides essentially in lowering the energy of activation of a chemical reaction or in the reaction being based on a chain mechanism involving catalysts. In most processes, the accelerating action of the catalyst consists in breaking a one-step process requiring a higher activation energy E into two (or more) steps, each step calling for an activation energy e_1, e_2, . . ., much lower than E. For example, synthesis may proceed without a catalyst as follows:

$$A + B \rightarrow AB \qquad (a)$$

with an activation energy E. In the presence of a catalyst, two consecutive reactions take place:

$$A + [Cat] \rightarrow A [Cat] \qquad (b)$$
$$B + A [Cat] \rightarrow AB + [Cat] \qquad (c)$$
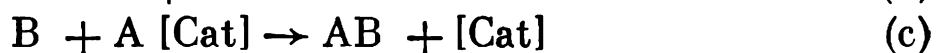
with lower activation energies e_1 and e_2.

In homogeneous catalysis, when the catalyst is in the same phase (gas or liquid) with the reactants, the intermediate compound A [Cat] may exist as a separate component that may be detected by chemical analysis. In heterogeneous catalysis, when, for example, a solid catalyst is in the liquid or gas phase including the reactants A and B, the intermediate substance A [Cat] is not a three-dimensional entity that can be detected by chemical analysis. A [Cat] is merely a surface compound (product of activated adsorption). However, even in heterogeneous catalysis the catalyst and reacting substances exchange electrons or protons. Therefore, catalysts are specific, that is they selectively accelerate some reactions without affecting the rate of the others.

Thus, for oxidation-reduction reactions, in which catalysts promote electron transitions in the reacting molecules at the expense of their own electrons, typical catalysts are metals and, to a lesser

extent, metal oxides. In the first step of a catalytic process (during formation of the A [Cat] complex), metals normally act as electron donors, while in the second step they accept electrons, thereby being regenerated as catalysts. Oxides of metals with a variable valence act in an opposite manner. For catalysis of oxidation-reduction reactions (oxidation, reduction, hydrogenation, dehydrogenation) most frequently used are metals of the eighth group of the periodic system and such oxides as Fe_2O_3, Cr_2O_3, and V_2O_5.

In the case of acid-base reactions (hydration, dehydration, hydrolysis, polymerization, polycondensation, cracking, etc.) in which the catalyst promotes ion (primarily proton) transitions, the typical catalysts are inorganic acids (proton donors), particularly phosphoric and sulphuric acids as the ones exhibiting low volatility at elevated temperatures. Al_2O_3, SiO_2, and aluminosilicates are also often used.

Predominant in the chemical industry is heterogeneous catalysis over solid contacts which represent a combination of catalyst, promoter, and support. Promoters may act chemically and physically. In the case of chemical action, promoters form more active compounds with the catalyst or participate, together with the catalyst, in activated adsorption. When acting physically, promoters provide for a most active microstructure of the catalyst. Supports exhibiting high strength and thermal stability ensure high porosity of the contact grains, hence an extended pore surface bearing tiniest crystals of both the catalyst and promoter. Contacts are used in the form of lumps resulting from crushing of a calcined material, or shaped spherical grains, granules, or pellets. Fine-grained, pulverized catalysts are employed in liquid-phase and some processes of gas-phase catalysis. In fast reactions involving highly active catalysts use is made of fine meshes fabricated from the catalytic metal: platinum, silver, or copper.

Homogeneous catalysis is less common, mainly because of the difficulties in separating the catalyst from the process mixture. Hydrogen, hydroxy and metal ions are predominantly used in liquid-phase homogeneous catalysis. In gas-phase catalysis of oxidation of methane to formaldehyde and partial oxidation of sulphur dioxide, nitrogen oxides perform the function of the homogeneous catalyst.

Catalytic reactions fall into a common pattern (Chapter 1); all formulas belonging to the kinetic region also apply to calculation of the corresponding parameters of catalytic reactions, and the same curves can be used.

In studying reversible catalytic processes in the gas phase with solid catalysts, one must first of all determine the dependence of the conversion of the main starting substance on temperature and contact time. In the case of exothermic reactions, these relationships take the form of the curves shown in Fig. 36.

The equilibrium curve is plotted from reference data ($(x_{eq} = f(T)$ or $K_{eq} = f(T)$). The $x = f(T)$ curves corresponding to different times of contact between the gas and catalyst ($\tau_1, \ldots, \tau_5$), all other parameters being constant, are derived from experimental data. Joining of the points of maximum yields, corresponding to optimal temperatures T_{opt}, gives an optimal curve. It indicates that as τ and x increase, the temperature must be lowered to attain maximum process rate and conversion. The experimental data can be verified using the following formula for an approximate determination of the optimal temperature:

$$T_{opt} = \frac{T_{eq}}{1 + \dfrac{2.3RT_{eq}}{mq_r} \log \dfrac{E + mq_r}{E}}, \qquad (2.1)$$

where T_{eq} is the thermodynamic temperature at equilibrium, which is determined from the equilibrium curve of Fig. 36; R is the universal gas constant, in J/(mole·K); m is a coefficient in the reaction equation, at the substance present in an amount less than the stoichiometric (limiting the reaction rate); q_r is the heat of the reaction, in J/mole; and E is the activation energy provided by the catalyst used.
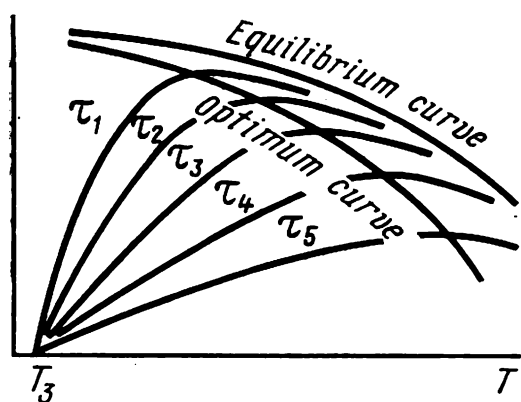
Fig. 36. Product yield x versus temperature in exothermic reaction at different contact times over a given catalyst: $\tau_1 > \tau_2 > \tau_3 > \tau_4 > \tau_5$ (P, C_1, C_2, . . .= const)

Equation (2.1) applies only to the kinetic region. In the presence of diffusion resistances, the experimental curve of optimal temperatures will be below that calculated from Eq. (2.1). The value of T_{opt} can be calculated from particular formulas available in reference books.

If the process occurs in the diffusion region, the rate constant determined from the experimental data depends on the diffusion coefficients or, in other words, is defined by Eq. (1.18).

A catalyst may augment the reaction rate to such an extent that the process as a whole passes from the kinetic to the diffusion region. In that case, the use of catalysts must be combined with more vigorous stirring.

Heterogeneous catalysis, just as every industrial chemical process, generally comprises three steps (stages): (1) transfer of the reacting substances into the reaction zone; (2) chemical reactions; and (3) removal of the products from the reaction zone. Such a scheme, however, is not sufficient to account for the mechanism of a process over solid porous catalysts. A catalytic process over porous grains is divided into the following steps: (1) diffusion of the starting reagents

from the gas (or liquid) flow toward the catalyst grain surface; (2) diffusion of the reagents inside the catalyst grain pores; (3) activated adsorption (chemisorption) of the reagents on the pore surface with formation of surface chemical compounds including the reagents plus the catalyst; (4) rearrangement of the atoms, resulting in formation of surface complexes: product-catalyst; (5) desorption of the product from the pore surface; (6) diffusion of the product in the pores; and (7) diffusion of the product from the grain surface into the flow core.

It is important that the diffusion of substances in the catalyst pores be unhindered in view of the fact that the surface of the pore walls is usually hundreds and thousands of times larger than the outer grain surface. It is usually attempted to select the gas (liquid) flow rate, catalyst grain size, and porosity such as to lift the limitations imposed by diffusion. If the attempts are successful, the overall process rate is determined by kinetic steps 3 through 5; more often than not their rates are commensurate with the result that the equation of the reaction has a fractional order.

As one passes from a less active catalyst to a more active one, the decrease in the activation energy usually brings down the reaction order. For example, in the case of oxidation of sulphur dioxide with oxygen according to the equation of reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + Q,$$
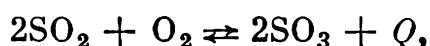
the kinetic equation of the forward reaction of homogeneous oxidation without a catalyst at current concentrations C_{SO_2} and C_{O_2} is of the third order:

$$\vec{u} = dC_{SO_3}/d\tau = kC_{SO_2}^2 C_{O_2}, \qquad (2.2)$$

the activation energy being $E \cong 280$ kJ/mole.

If a low-activity ferric oxide catalyst (Fe_2O_3) is used, the order of the forward reaction is 2.5:

$$\vec{u} = dC_{SO_3}/d\tau = k_{cat} \left(C_{SO_2}/C_{SO_3}\right)^{1.5} C_{O_2} \qquad (2.3)$$

at $E_{cat} = 160$ kJ/mole.

In the case of vanadium catalysts with promoter K_2O, used under normal catalysis conditions, the overall approximate equation with due account for the forward and back reactions corresponds, according to Boreskov, to the order 1.8 at $E_{cat} = 92$ kJ/mole:

$$u = \frac{dC_{SO_3}}{d\tau} = k'_{cat} \left(\frac{C_{SO_2} - C_{SO_2}^*}{C_{SO_3}}\right)^{0.8} C_{O_2}, \qquad (2.4)$$

where $C_{SO_2}^*$ is the equilibrium concentration of SO_2 and C_{SO_3} is the current concentration of SO_3.

Finally, when the most active platinum catalyst (metallic platinum) is used, the reaction is of the zeroth order with respect to oxy-

gen and, generally, of the first order at $E_{cat} \cong 68$ kJ/mole:

$$\frac{dC_{SO_3}}{d\tau} = k''_{cat} \frac{C_{SO_2} - C^*_{SO_2}}{C^{0.5}_{SO_3}} .$$ (2.5)

The catalyst activity A is usually defined as the ratio between the rate constant k_{cat} of a reaction with a catalyst and the rate constant k of a reaction without a catalyst:

Fig. 37. Catalyst activity A as a function of decreasing activation energy $\Delta E = E - E_{cat}$

$$A = \frac{k_{cat}}{k} = \frac{e^{-E_{cat}/RT}}{e^{-E/RT}} = e^{\Delta E/RT},$$ (2.6)

where $\Delta E = E - E_{cat}$.

As ΔE increases, the catalyst activity goes up along an exponential curve (Fig. 37).

The rate constant k_{cat} of a catalytic process and the catalyst activity are determined, primarily, by the nature of the reacting substances and the specificity of the catalyst. However, under different conditions in the kinetic or diffusion region, the catalyst activity is a function of many process parameters:

$$A = f (C_{cat}, C_{prom}, C_{s.\,s}, C'_{s.\,s}, C_{pr}, C_{imp}, t,$$

$$S_{sp}, d_{gr}, r_p, M_{s.\,s}, M'_{s.\,s}, M_{pr}, \mu, \rho, w),$$ (2.7)

where C is the concentration of, respectively, the catalyst (cat), promoter (prom), starting substances (s.s), product (pr), and impurities (imp); t is temperature; S_{sp} is the specific surface of the catalyst; d_{gr} is the mean grain size (diameter); r_p is the equivalent pore radius; M stands for the molecular weights of the starting substances (s.s) and product (pr); μ is the viscosity of the medium; ρ is density; and w is the linear velocity of the reagent flow.

The effect of each parameter on activity can be observed experimentally only provided the other parameters are constant. The effect of the catalyst concentration C_{cat} manifests itself in homogeneous catalysis as shown by curve *1* of Fig. 38. If the catalyst is in great excess in comparison with the stoichiometric equation of reaction
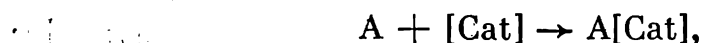
$$A + [Cat] \rightarrow A[Cat],$$

increasing its concentration further does not produce any effect on the process rate. Thus, the kinetic equation of a catalytic reaction of the $A + B + [Cat] \rightarrow AB + [Cat]$ type takes the form

$$u = kC_A C_B C^m_{cat},$$ (2.8)

where m decreases from 1 to 0 as the excess amount of the catalyst increases. In heterogeneous catalysis, the catalyst is almost invar-

iably present in an excess amount; in calculations it is assumed that $m = 0$.

The promoter concentration C_{prom} follows curve *2* (see Fig. 38) in heterogeneous catalysis, and an excess amount of the promoter may cause screening of the catalyst on the grains, thereby reducing its activity.

The activity of a catalyst is not a continuous function of the reagent concentrations $C_{s.s}$ and $C'_{s.s}$, however, a marked increase or
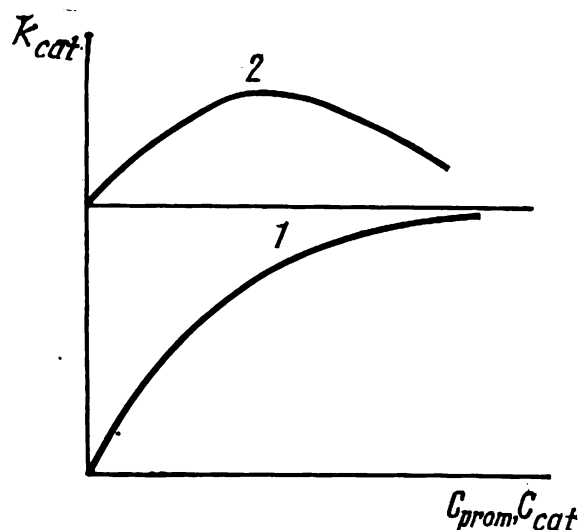
Fig. 38. Reaction rate constant versus catalyst (1) and promoter (2) concentration
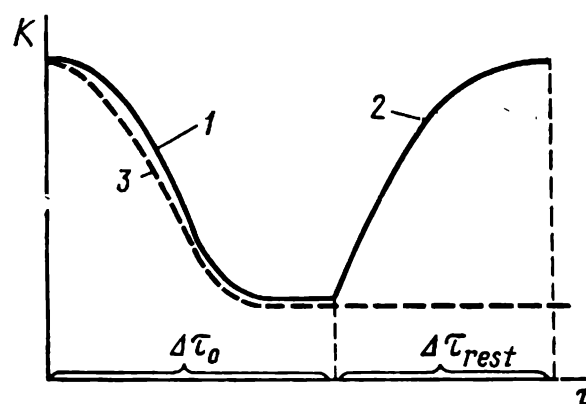
Fig. 39. Reaction rate constant versus time

1—reversible poisoning; *2*—activity restoration; *3*—irreversible poisoning; $\Delta\tau_0$—poisoning time; $\Delta\tau_{rest}$—restoration time (reaction mixture is free of poison)

decrease in the concentration of one of the reagents may affect the mechanism of the process and, consequently, the kinetic equation. In addition, new chemical compounds of the catalyst with the reagent may appear in the form of individual crystals, which is accompanied by a change (usually an increase) in the activation energy.

A substantial increase in the product concentration C_{pr} may alter the mechanism of the process, just as that in $C_{s.s}$ would do. However, in autocatalytic processes the formation of the product speeds up the reaction. In many catalytic processes over solid catalysts, an increase in the product concentration slows down the reaction (see, for example, Eqs. (2.3) through (2.5)) since the overall process rate is influenced by the rate of product desorption from the active centres or by the rate of product diffusion inside the grain pores.

An increase in the impurity concentration C_{imp} may produce different effects. If the concentration of impurities inert with respect to the catalyst increases, the process rate slightly decreases. Catalyst poisons may cause a sharp drop in the catalyst activity. In the case of reversible poisoning (curve *1* of Fig. 39), the catalyst activity decreases to a certain level corresponding to the poisonous impurity

concentration, then, as the poisoning time increases further, the activity remains the same. When the poison is excluded from the reaction mixture, the catalyst activity is restored along curve *2*. When poisoning is irreversible (curve *3*), the activity is not restored after the poison is eliminated from the reaction mixture. The degree of poisoning is calculated from the ratio of the rate constants over poisoned (k_{pois}) and fresh (k_{fr}) catalysts at a given temperature:

$$\alpha_{pois} = k_{pois}/k_{fr}. \tag{2.9}$$

The effect of temperature in the kinetic region is determined by the Arrhenius equation

$$k = k_{pois}e^{-E/RT}, \tag{2.10}$$

which is usually reduced to the following form convenient in calculations:

$$2.3 \log \frac{k_2}{k_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{2.11}$$

or

$$\log k = B - A/T, \tag{2.12}$$

where k, k_0, k_1 and k_2 are the reaction rate constants at the corresponding temperatures T, T_0, T_1, and T_2; e is the base of natural logarithms; $A = E/2R$ and $B = \log k_0$ are coefficients constant for the reaction under consideration (within the limits of constancy of the temperature coefficient β of the reaction).

Knowing E and k_1 at temperature T_1, one can calculate k_2 at T_2 from Eq. (2.10) or (2.11), then determine the temperature coefficient of the reaction rate

$$\beta = (k_T + 10)/k_T. \tag{2.13}$$

On the average, $\beta_{av} \cong 3$ for catalytic reactions, but this coefficient increases by one order of magnitude with decreasing temperature and increasing activation energy.

If the coefficients A and B are known for the reaction involved, the rate constant can be easily determined on a plot. On the other hand, if the rate constants k_1 and k_2 at two temperatures T_1 and T_2 have already been determined, Eq. (2.11) is used to find the activation energy (see Fig. 21). For processes in the diffusion region $k = f(D)$ and for gas-phase processes $\beta_{av} = 1.2$.

The relationship between activity, on the one hand, and the specific catalyst surface S_{sp}, grain size d_{gr}, and equivalent pore radius r_p, on the other, must be considered as a whole. When catalysis proceeds in the kinetic region,

$$A = a_1 S_{sp}, \tag{2.14}$$

but in the case of a catalyst having a uniform porous structure,

$$S_{sp} = a_2/r_p, \qquad (2.15)$$

where a_1 and a_2 are proportionality factors.

Hence, it would be appropriate to reduce the pore sizes. However, in the case of large catalyst grains ($d_{gr} > 2$ mm) typical of fixed-bed reactors, as r_p diminishes, the overall catalysis rate slows down due to the internal diffusion resistance, which is why catalysts with large pores have to be used. The effect of S_{sp}, r_p, and d_{gr} on the catalyst activity is illustrated in Fig. 40 in which the horizontal portions
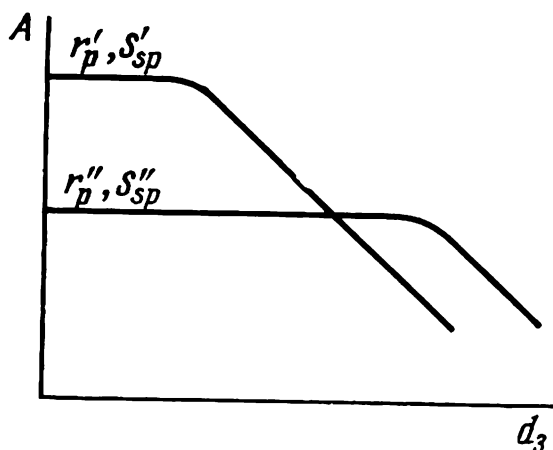
Fig. 40. Catalyst activity versus grain size at different pore sizes: $r_p' < r_p''$; $S_{sp}' > S_{sp}''$
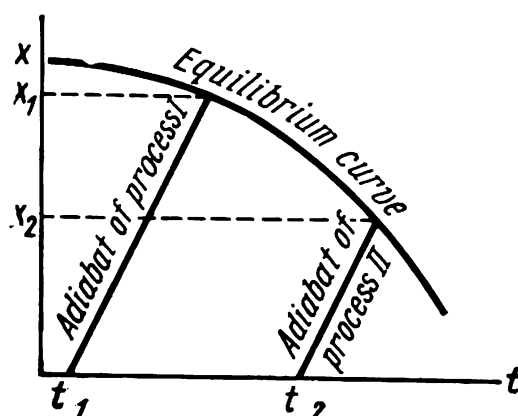
Fig. 41. Adiabats of exothermic reaction in the filter bed of a single-tray catalytic reactor

of the curves correspond to the kinetic region and their sloping portions, to the diffusion region.

The effect of the molecular weights $M_{s.s}$, $M_{s.s}'$, and M_{pr} of the starting substances and the product in the external and internal diffusion regions can be described in the following terms:

$$D = a/\sqrt{M}, \qquad (2.16)$$

where D is the diffusion coefficient. The overall rate of the diffusion process will be limited by the component with the highest molecular weight.

An increase in the viscosity μ and density ρ of the reagent flow reduces the diffusion rate. Increasing the reagent flow rate w minimizes or eliminates completely the external diffusion resistances and, at the same time, decreases the driving force of the process as a result of axial mixing of the starting substances with the reaction products. The degree of axial (longitudinal) mixing is usually disregarded in the value of the driving force (in the formulas of formal kinetics), hence, in calculations of the rate constant based on experimental data, it results in a formal decrease in k. The apparatus diameter D_{ap}, catalyst bed height H, and other geometric parameters

affect the rate constant through the hydrodynamics of the process and, more particularly, through the degree of mixing of the reagents in the flow.

Increasing the catalyst activity in high-temperature gas-phase reactions not only augments the reaction rate under given conditions but also reduces the minimal temperature of the reaction mixture at which the reaction starts proceeding at a rate adequate for the industrial process and which is known as the ignition temperature. By lowering the latter one can cut down the size of the apparatus serving to preheat the reacting gases, save on power consumption, and enhance the yield of the product of the exothermic reaction in the filter catalyst bed. In tray-type catalytic reactors with a filter bed, the temperature rises adiabatically, almost proportionally with the percentage conversion (Fig. 41), and at a low ignition temperature t_{ign_1} the percentage conversion x_1 may be maximum, higher than x_2 at a high ignition temperature t_{ign_2}.

LABORATORY WORK 12. CATALYTIC CRACKING OF PETROLEUM PRODUCTS

Currently, catalytic cracking is one of the most important refining processes. Conversion of pertroleum products over catalysts provides for a high yield of petrol with an octane number as high as 85, kerosene-gas oil fractions (fuel for diesels and gas turbines), and gas containing a great amount of saturated and unsaturated hydrocarbons C_3—C_4, widely used in commercial organic synthesis. The selectivity of catalysts, dependent on the chemical composition and structure, determines the ratio of yields of various products (gas, petrol, coke) and their composition.

As opposed to steam cracked petrol (see Work 9), the catalytically cracked one is characterized by a much greater stability owing to the absence of diene compounds and sulphur and exhibits a superior knock resistance due to the high content of isoalkanes and aromatics.

Catalytic cracking is normally conducted in the vapour phase at temperatures ranging from 450 to 520 °C, at a pressure of 0.1 to 0.2 MPa, and at a contact time of several seconds. Under these conditions catalytic reactions are much faster and more complex than the reactions involved in thermal cracking. The most important, apart from the decomposition reactions, are the reactions of isomerization and redistribution of hydrogen, which are responsible for the high quality of cracking products, as well as the condensation processes resulting in formation of coke and its deposition on the catalyst. The rates of the above reactions are different depending on the hydrocarbon species. The most reactive are olefinic hydrocarbons. Although catalytic cracking belongs to highly complex processes, its initial steps, that is formation of the primary reaction products

(the decomposition rate of individual hydrocarbons) can be approximately described by Eqs. (1.23) and (1.24) for plug-flow conditions

$$u = \frac{dx}{d\tau} = k\,\Delta C = k\,(1-x), \quad k = \frac{1}{\tau}\ln\frac{1}{1-x}$$

and Eqs. (1.27) and (1.28)

$$u = \frac{x}{\tau} = k\,(1-x), \quad k = \frac{1}{\tau}\frac{x}{1-x}$$

for mixing conditions.

The overall reaction rate constant will be determined not only by the relative rate of decomposition of saturated hydrocarbons but also by the rate of condensation of the unsaturated ones. Under conditions more favourable for the last reaction, the cracking rate will be cosistent with the equation for a reaction of an order intermediate between the first and second ones.

The cracking reaction involves a radical-chain mechanism, catalytic cracking proceeding via carbonium ions. The most reactive are tertiary carbonium ions conducive to formation of isoparaffins. Catalytic cracking products differ in composition and properties. For example, petrol contains many isoparaffins and aromatic hydrocarbons, gas has a high content of isobutane and unsaturated hydrocarbons, while gas oil fractions contain a great amount of polycyclic and aromatic hydrocarbons. Depending on the fractions present in the stock, composition and size of the catalyst grains, and process temperature range, the cracking process occurs in the kinetic or diffusion region. In the case of a diffusion resistance to cracking, introduced into Eq. (1.23) is a term representing the slowing down of the process, then the rate constant is given by

$$k = \frac{1}{\tau}\ln\frac{1}{1-x} - \beta x, \tag{2.17}$$

β being this term.

The following are the factors determining the yield and quality of cracking products: type of raw materials, composition and activity of the catalyst, process temperature and pressure, as well as the space velocity of the stock fed into the reactor and the duration of continuous cracking without regeneration of the catalyst. In catalytic cracking use is made of catalysts differing in composition and the way in which they are prepared. The quality of the catalyst used and the cracking process conditions determine the direction of chemical conversion of the fuel. For example, when a catalyst containing, primarily, Al_2O_3 and SiO_2 is used, naphthene hydrocarbons decompose and polymerize. Finely porous catalysts are responsible for a high yield of gas in view of the fact that their surface is less accessible to the molecules of the starting materials. Besides, coarse-pored catalysts are easier to regenerate than the fine-pored ones,

with a minimal loss of activity. Therefore, the industry prefers using coarse-pored catalysts, particularly if the stock is heavy.

Catalysts for catalytic cracking are produced from natural clays (of the floridin type) or synthesized. For example, amorphous aluminosilicate catalysts result from coprecipitation of aluminium hydroxide and silica from solutions of respective salts with subsequent hydration. In some cases, they exhibit high activity without any additives, although active components are often applied on them.

The chemistry of conversion of paraffin hydrocarbons during cracking can be represented as the main reactions of decomposition of heavy paraffins and secondary reactions of isomerization, cyclization, alkylation, and others. For example, for dodecane the main decomposition reactions are

$$C_{12}H_{26} \rightarrow C_6H_{14} + C_6H_{12}$$
$$C_{12}H_{26} \rightarrow C_5H_{12} + C_4H_8 + C_3H_6$$
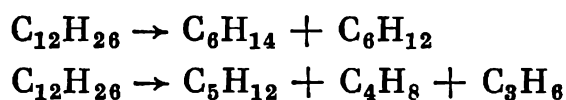
The secondary reactions may include

$$CH_3CH_2CH_2CH_2CH{=}CH_2 \xrightarrow{\text{isomerization}} CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH{=}CH_2$$

$$C_6H_{12} \xrightarrow{\text{cyclization}} \begin{matrix} & CH_2 & \\ H_2C & & CH_2 \\ H_2C & & CH_2 \\ & CH_2 & \end{matrix} \xrightarrow{\text{dehydrogenation}} C_6H_6 + 3H_2$$

$$C_6H_6 + C_3H_6 \xrightarrow{\text{alkylation}} C_6H_5CH\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$
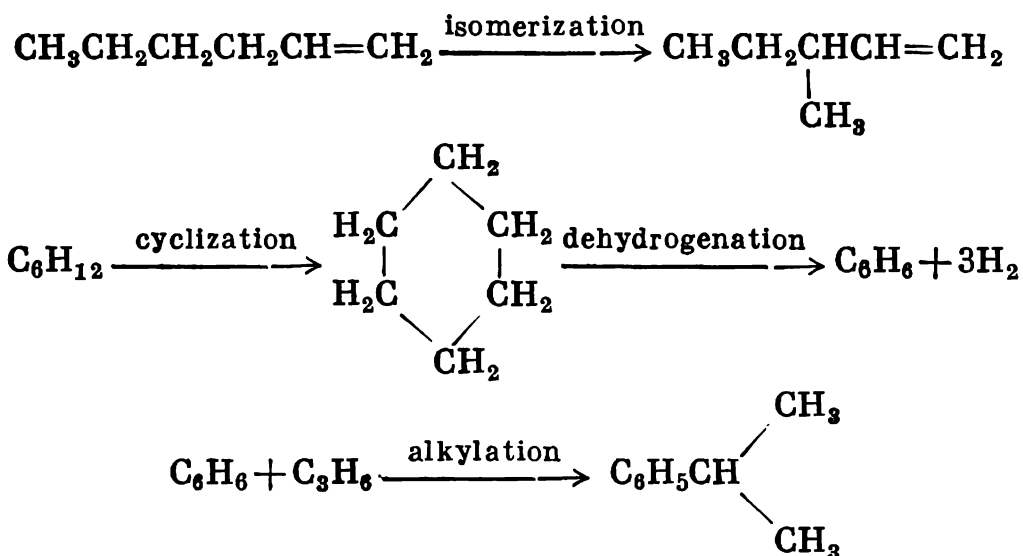
The decomposition products of naphthenes also enter into the secondary reactions of isomerization and dehydrogenation, yielding aromatic hydrocarbons. As a result, in catalytic cracking, the multiple bond shifts, the structure of the carbon skeleton changes, and the saturation of double bonds is followed by cyclization and alkylation. The most important factor in cracking is temperature which determines the degree and rate of catalytic decomposition of hydrocarbons, especially that the cracking action of the catalysts occurs within a narrow temperature interval. Raising the temperature intensifies the process of hydrocarbon decomposition. Since cracking proceeds in the adsorption layer on the catalyst surface rather than inside the catylyst, the effect of pressure is insignificant. Increasing the pressure promotes polymerization, hydrogen redistribution, and coke formation. However, in industrial processes the pressure is manipulated but to a small extent. The cracking results also depend

on its duration. The space velocity of the fed liquid stock in catalytic cracking usually varies from 0.1 to 10 $dm^3/h \cdot m^3$ of the catalyst (the most common velocities are 0.5 to 2.0 $dm^3/h \cdot m^3$ of the catalyst at 0 °C); the lower the space velocity, the greater the cracking intensity, all other things being equal.

As a result of coke deposition, the activity of the catalyst diminishes in the course of time, and it has to be regenerated. The regeneration of the catalyst is done by blowing air through it at 550 to 600°C to burn off the coke. The continuous cracking time between catalyst regenerations materially affects the results of the process. It ranges from 1.5 to 10 min. The shorter the catalysis time, the higher the mean activity of the catalyst within this period.

The source of the coke depositing on the catalyst is, primarily, the resinous and asphaltic substances present in the raw material. The catalyst regeneration process is, as a rule, more complicated than the cracking itself. It releases a lot of heat—anywhere from 25 to 31 thousand kilojoules per kilogramme of coke. At moderate temperatures (450 to 500 °C), the regeneration proceeds in the kinetic region, and its rate is determined by that of the oxidation reaction. However, as the temperature rises up to 550 °C, the regeneration process enters the diffusion region.

The cracking products include gas, petrol, kerosene-gas oil fraction, cracking residue, and coke. The yield of gas is 4 to 7%, on the average, while that of petrol is 40 to 45%. The chemical composition of petrol is approximately as follows: naphthene hydrocarbons—20 to 25%; unsaturated hydrocarbons—5 to 6%; paraffin hydrocarbons—45 to 50%; and aromatic hydrocarbons—20 to 25%. The catalytically cracked gas oil is successfully used as diesel fuel or subjected to thermal cracking. The amount of the coke depositing on the catalyst usually varies from 1 to 5% depending on the raw material and process temperature.

Students embarking upon this work must determine the yield of the main catalytic cracking products and analyze them.

Experimental Setup and Procedure

The experimental setup for catalytic cracking (the raw material consumption rate being 150 to 200 cm^3/h) is illustrated in Fig. 42. A reactor *1* is a refractory glass tube 25 to 35 mm in diameter and 500 to 550 mm high. The catalyst is loaded onto the glass packing layer in the lower part of the tube. Another layer of glass packing covers the catalyst for evaporation of the raw material fed into the reactor on it. On the outside, the reactor is heated by an electric coil *2* wound over an asbestos insulating jacket. The coil is made of nichrome wire 0.8 to 1.0 mm in diameter wound around the tube at equal pitches over the asbestos sheet 0.5 to 1 mm thick. The winding pitch

is 0.75 to 1.0 cm at the 500-mm level. The tube *1* has rubber plugs on top and at the bottom. The top plug accommodates a burette *4* with a stopcock *3*, receiving the starting material, and a thermocouple *7*. Into the bottom plug is inserted a tube through which the reaction products are discharged from the reactor into a cooler *9*. The capacity of the burette *4* is 300 to 400 cm³.

The stopcock *3* of the burette is preadjusted to a particular rate of feeding the stock into the reactor (a calibrated capillary may be
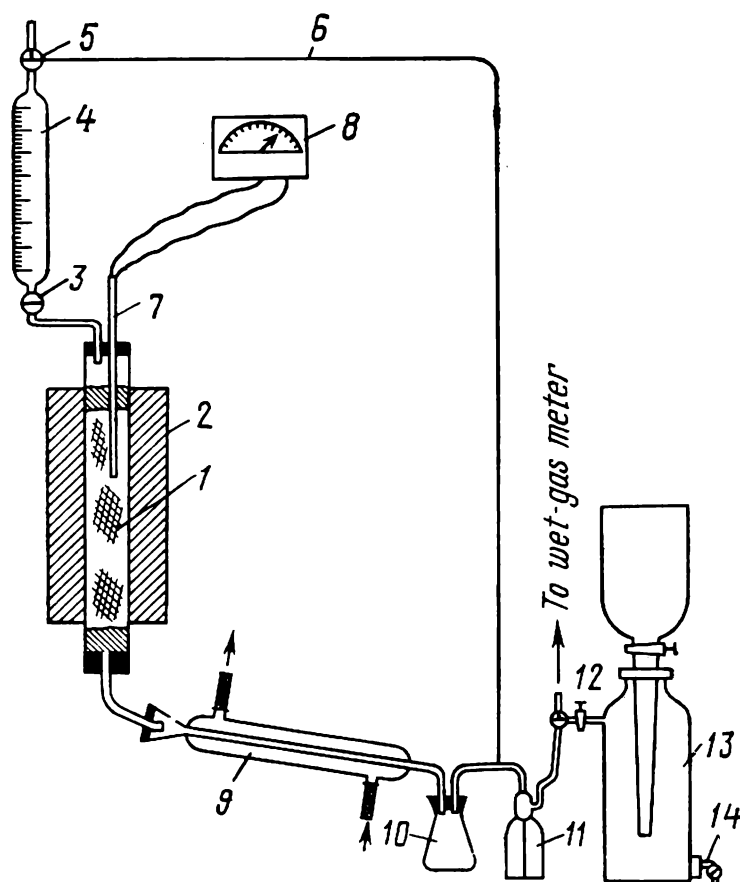
Fig. 42. Experimental setup for catalytic cracking

used instead). On top, the burette is provided with a three-way valve *5* through which it communicates with the atmosphere (while the starting material is being charged into the burette) and with a line *6* equalizing the pressure in the system (for the duration of the experiment). The water cooler *9* is intended for cooling and condensation of the vapours emerging from the reactor. A receiver *10* admitting the cooled condensate and cracking gas is intended for collection of the liquid distillate. It is essentially an ordinary glass flask. The gaseous products from the receiver *10* are fed into an absorption flask *11* serving to absorb petrol, the absorbent being solar oil. The level of the solar oil in the absorption flask must be as low as possible (3 to 5 cm) to minimize the resistance of the system. The cracking gas passes through a gas meter (not shown) into an exhaust hood where

it is burnt. Arranged in parallel with the gas meter is a gas holder *13* filled with a saturated sodium salt solution, in which gas is sampled for analysis. If it so specified in the assignment, the gas may be sampled for analysis in the course of the experiment with the aid of a three-way valve *12*. During sampling, the liquid flows out of the gas holder through a cock *14*. If the gas holder is big enough, it can also serve as a collector of the gaseous products from the absorption flask. If the system includes a gas meter, the gas is fed into the gas holder in the middle of the experiment after air has been bled from the system. The thermocouple *7* with a millivoltmeter *8* measures the temperature inside the reactor.

The experimental conditions are defined in the assignment which specifies the raw material, process temperature, space (or mass) velocity of the raw material fed into the reactor, the duration of cracking without regeneration of the catalyst, and other parameters. The raw material feed rate depends on the amount of the loaded catalyst and is preset equal to 0.5 to 2.0 volumes of the stock per volume of the catalyst per hour (at 0 °C). The duration of the experiment is selected such as to ensure a sufficient amount of the liquid product for subsequent determinations of the yields of petrol, ligroin, and gas oil (100 to 150 cm³). An amount of 100 to 150 cm³ of the catalyst being loaded into the reactor and the space velocity being equal to 2 volumes of the stock per volume of the catalyst per hour, the experiment may last not longer than an hour. The temperature in the reactor should preferably be maintained within 450 to 500 °C by means of a rheostat.

When fresh catalyst (not yet regenerated) is used in the experiment, it must first be dehydrated. To this end, the reactor is heated to 300-350 °C, and the catalyst is blown with air with the aid of an air blower connected to the reactor instead of the burette *4*. The blowing is carried out as long as may be required for complete evaporation of the water drops appearing at the beginning of blowing on the inner walls of the glass tube connecting the reactor with the cooler.

Prior to the experiment, the burette must be filled with the raw material, the gas holder is filled with brine, and the joints between individual components of the setup are tested for air-tightness. For the latter test, the stopcock of the burette is closed, while the cock of the gas holder is opened. If the system is completely airtight, the liquid stops flowing out of the gas holder after several minutes. Otherwise, the leaky joints must be sealed and the air-tightness test must be repeated. The experiment starts only after the entire system has been rendered airtight. First, the heating coil of the reactor is energized. After the temperature in the reactor has reached 300-400 °C, the system must be again checked for air-tightness when hot. As soon as the reactor temperature exceeds the predetermined level

by 5 to 10° (this normally takes 20 to 30 min), the feeding of the raw material starts. But first, the feed rate must be adjusted to one or two drops per second (according to the assignment). Then, the temperature is maintained at the desired level with the aid of the rheostat, and the liquid level in the burette and temperature are registered every five minutes beginning from the instant at which the raw material starts being fed in. The results are entered in the following table:

Time	Millivolt-meter reading, mV	Tempera-ture, °C	Amount of raw material in the burette, cm³	Remarks
Experiment begins at ——— h ——— min 5 min 10 min . . . . Experiment ends at ——— h ——— min				

If the experiment lasts longer than an hour, the catalyst must be regenerated every hour. At the same intervals, just as after the experiment, the resins and coke deposited on the catalyst during the experiment must be burnt off. The catalyst is regenerated without switching off the heating coil, and the air blower is connected by means of a hose to the upper glass tube of the reactor, instead of the feeding burette *4*. The rate of air flow into the reactor during the regeneration is 20 to 30 dm³/h, and the temperature must not exceed 500-520 °C. The regeneration usually lasts one to three hours depending on the thickness of the deposit. The combustion products are collected in the gas holder. As soon as the gas holder is filled with gas, the latter is sampled for analysis to determine the CO_2 content. The gas is then discharged from the gas holder which is again used as a collector. The regeneration discontinues when the CO_2 content in the gas does not exceed 0.5%. (The gas in the first two or three gas holders must also be analyzed for CO content to more accurately determine the amount of combustion products.) Instead of being delivered into the gas holder, the gas may be directed into the exhaust hood (with the aid of the valve *12*) with periodic sampling.

The end of regeneration is indicated by the absence of turbidity when the gas emerging from the reactor is passed through lime water. Another indication of the end of regeneration is the temperature drop in the furnace. The catalytic cracking process ends in determination of the yield of liquid products, gas and coke. The liquid

product yield A is found by weighing the receiver *10* and absorption flask *11* before and after the experiment and calculated using the formula

$$A = G_f - G_0 + (G_{ab.f} - G_{ab.0}),$$

where G_f is the weight of the receiver after the experiment, G_0 is same before the experiment, $G_{ab.f}$ is the weight of the absorption flask after the experiment, and $G_{ab.0}$ is same before the experiment. A material balance is drawn up (if it is stipulated by the assignment) from the yields of all products—gaseous, liquid, and solid.

The liquid products are poured into a flask with a rod-and-disc type fractionating tube and distilled. The flask is weighed before and after loading. The distillation products are collected in pre-weighed receivers. The product is distilled into a petrol fraction boiling away at a temperature of up to 170 °C and a ligroin fraction boiling away within the range of 170 to 230 °C. The residue in the flask is catalytically cracked gas oil. If only a part of the total amount of the liquid products (distillate) is taken for distillation, the yield of each fraction must be recalculated with respect to the entire distillate. Besides, added to the weight of the petrol fraction must also be the weight of the light fractions absorbed in the absorption flask. The yields of petrol, ligroin, and gas oil are expressed as percentage of the total amount of the consumed stock. The volume of the resulting gas is determined from the readings of the gas holder or gas meter. The weight of the gaseous cracking products is determined from the gas volume and density (see Work 36).

The amount of the coke residue forming during the experiment is calculated on the basis of the quantity of the combustion products resulting from catalyst regeneration, as well as the content of carbon dioxide in these products. The total volume of CO_2 in the combustion products at the specified temperature and pressure is calculated as follows:

$$V = \frac{v_1 a_1 + v_2 a_2 + v_3 a_3 + \ldots + v_i a_i}{100}, \qquad (2.18)$$

where V is the total volume of CO_2, in dm³; v_1, v_2, v_3, . . ., v_i stand for the volumes of the gas filling the first, second, third, and ith gas holders, in dm³; and a_1, a_2, a_3, . . ., a_i stand for the CO_2 content in the gas filling the first, second, third, and ith gas holders, respectively, in %.

Hence, the amount of coke (in g) will be

$$G_{coke} = \frac{V_{273} P_{12}}{(t + 273) \, 760 \cdot 22.4}, \qquad (2.19)$$

where P is the atmospheric pressure, in Pa, and t is the gas temperature in the gas holder, in °C.

The experimental results are to be tabulated as follows:

Stock	Experimental conditions			Raw material consumption, g	Product yield										
	duration, min	temperature, °C	space veloc- ity, h⁻¹		liquid product		absorbent weight incre- ment		gas		coke		Losses		
					g	%	g	%	g	%	g	%	g	%	

After the experiment, the gaseous and liquid products are analyzed to determine their composition. The content of unsaturated hydro-carbons is determined by the method described in Work 9. The entire gas mixture is analyzed with the aid of gas analyzers using the method described in Work 36 and chromatographically as described in Work 37.

LITERATURE

Magaril, R. Z., *The Basic Theory of the Chemical Processes Involved in Oil Refining*, Moscow, 1976, p. 312.

Belyanin, B. V. and Erikh, V. N., *Proximate Analysis of Petroleum Products and Gas*, 2nd revised and expanded edition, Leningrad, 1975, p. 335.

Instructions to the Laboratory Work "Catalytic Cracking of Petroleum Products"

1. Switch on the heating of the reactor and fill the burette with the starting material.
2. As soon as the prescribed temperature is reached, switch on all the traps and exhaust hoods and start feeding the stock at a constant rate.
3. Conduct the process under an exhaust hood and wearing goggles.
4. After the experiment, switch off the heating of the reactor, disconnect the receiver and absorption flask, and weigh them.
5. Analyze the resulting gaseous and liquid products to determine their composition.
6. Regenerate the catalyst.
7. Determine, from the analysis data, the yields of petrol, ligroin, and gas oil as the percentage of the total amount of the stock consumed.

LABORATORY WORK 13. CONTACT OXIDATION OF SULPHUR DIOXIDE

The homogeneous oxidation of sulphur dioxide to sulphur tri-oxide proceeds according to the equation

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + Q$$
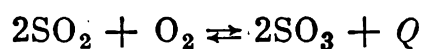
However, the homogeneous third-order gas-phase reaction is extreme-ly slow, which is why in the production of sulphuric acid sulphur dioxide is oxidized in a contact process over catalysts. In accordance

with Boreskov's kinetic equation, the overall rate of oxidation over a vanadium catalyst (V_2O_5 with promoter K_2SO_4) varies with the eight-tenths power of the sulphur dioxide concentration and linearly with the oxygen concentration. Hence, the reaction is of a fractional (1.8) order. The thermal effect Q of the reaction (J/mole) as a function of temperature is determined by the equation

$$Q = 101\ 400 - 9.26T. \tag{2.20}$$

Since the formation of sulphur trioxide is accompanied by evolution of heat, its equilibrium yield or the degree of sulphur dioxide oxidation, decreases with increasing temperature. The equilibrium of this reaction as a function of temperature is characterized by the following values of the equilibrium constant:

Temperature, °C	400	450	500	550	600
$K_1 = \sqrt{K_{eq}} = \dfrac{p_{SO_3}}{p_{SO_2} p_{O_2}^{0.5}}$	440	138	50.2	20.7	9.41

where K_{eq} is the usual equilibrium constant; K_1 is the equilibrium constant adopted in the production of sulphuric acid; p_{SO_3}, p_{SO_2}, and p_{O_2} are the partial pressures of the respective components at equilibrium.

The theoretical or equilibrium yield of sulphur trioxide (x_{eq}), as a function of the reagent concentration, is determined as follows for a respective temperature (a respective value of the equilibrium constant):

$$x_{eq} = \frac{K_1}{K_1 + \sqrt{\dfrac{100 - 0.5ax_{eq}}{P\,(b - 0.5ax_{eq})}}}, \tag{2.21}$$

where P is the total gas pressure, in Pa (usually $P = 1.01 \cdot 10^5$ Pa = = 1 atm); a is the SO_2 content in the gas mixture before oxidation, in % by volume; and b is the oxygen content in the same mixture, in % by volume.

The equilibrium yield of sulphur trioxide at atmospheric pressure, calculated for a mixture containing 7% of SO_2, 11% of O_2, and 82% of N_2, is as follows:

Temperature, °C	400	450	500	550	600	650
$x_{eq} \cdot 100$, %	99.25	97.64	93.80	86.16	73.85	58.50

At 400 °C and lower temperatures, the reaction of sulphur dioxide oxidation is virtually irreversible. At a temperature in the neighbourhood of 1000 °C, sulphur trioxide almost completely dissociates into sulphur dioxide and oxygen. Consequently, from the standpoint of completeness of conversion of sulphur dioxide to sulphur trioxide, the temperature should preferably be as low as possible. How-

ever, another factor that must be taken into consideration apart from the completeness of conversion is the reaction rate. At 400 °C, the reaction of sulphur dioxide oxidation proceeds at a rate satisfactory for an industrial process only over a platinum catalyst which is the most active of all catalysts.

At present, the industry uses the vanadium catalyst over which the oxidation of sulphur dioxide proceeds at a sufficiently fast rate at temperatures above 440 °C.

The rate of the sulphur dioxide oxidation reaction depends on temperature, catalyst activity, and concentration of the reagents. An increased pressure enhances the equilibrium yield and augments the reaction rate but the power consumed to compress the gas is not economically justified by the higher yield. Application of pressure is worthwhile only when oxygen is used to burn sulphur with subsequent processing of sulphur dioxide into sulphuric acid in a waste-free closed-loop system.

The rate of the sulphur dioxide oxidation reaction over the vanadium catalyst under conditions approaching plug flow is given, according to G. K. Boreskov, by the equation

$$u = kp_{O_2} \frac{p_{SO_2}}{p_{SO_2} + Ap_{SO_3}} \left[1 - \left(\frac{p_{SO_3}}{p_{SO_2} p_{O_2}^{0.5} K_{eq}} \right)^2 \right]. \qquad (2.22)$$

At percentage conversions exceeding 0.6, the following approximate equation may be used:

$$\frac{dx}{d\tau} = \frac{k}{a} \left(\frac{x_{eq} - x}{x} \right)^{0.8} \left(b - \frac{ax}{2} \right) \beta, \qquad (2.23)$$

where k is the reaction rate constant; x is the actual percentage conversion; β is a correction factor determining the concentration increment due to the reduction in the total volume of the gas mixture as a result of the reaction; and A is a constant; for a mixture containing 7% of SO_2 and 11% of O_2, $A = 0.7$.

The following values of the reaction rate constant, derived in an experiment with a vanadium catalyst from Eq. (2.23), can be shown by way of an example:

Temperature, °C	450	500	550	600
Rate constant	1.05	2.90	7.08	15.68

These data indicate that the reaction rate constant increases with temperature, while the equilibrium constant and, respectively, the equilibrium degree of oxidation of sulphur dioxide to sulphur trioxide decrease. Hence, to each degree of oxidation there corresponds an optimal temperature at which the rate is maximum. For the reaction to proceed at a maximal rate, it should be conducted with the temperature being constantly lowered, as sulphur dioxide is being converted to sulphur trioxide, along the curve of optimal tempera-

tures, passing through the points of maximal rates. The optimal temperature for a given percentage conversion is calculated approximately using the general equation (2.1) or the equation

$$T_{\text{opt}} = \frac{4905.5}{\log \dfrac{x}{(1-x)\sqrt{\dfrac{b-0.5ax}{100-0.5ax}+4.937}}} \cdot \qquad (2.24)$$

In modern fixed-bed catalytic reactors the gas passes successively through several (4-5) beds of the contact for the temperature to approach the optimum. The gas is cooled in heat exchangers between the beds for the temperature to go down as the degree of SO_2 oxidation increases. In spite of the continuous improvements in their design, fixed-bed catalytic reactors suffer from a number of disadvantages that do not allow further intensification of the contact sulphur dioxide oxidation process. They can operate only with coarse-grained granulated catalysts, the minimum size of the granules being not less than 4-6 mm. As a result, the pores of the catalyst are not used to a full extent, only 30% of them being involved in catalysis in the first bed. The temperatures at each step of catalysis depart far from the optimum because of the impossibility to abstract heat. The hydraulic resistance grows considerably during operation because of contamination of the catalyst bed.

The use of catalysts in a fluidized bed permits obviating the above drawbacks, to say nothing of the fact that the design of catalytic reactors is greatly simplified. In a fluidized-bed reactor use is made of a fine-grained vanadium catalyst whose particles are 1.0 to 1.5 mm in diameter, which allows both the inner and outer surfaces of the catalyst to be fully utilized. An important advantage of a fluidized catalyst bed is the rapid equalization of temperatures throughout the bed owing to the non-stop motion of the particles, which enables heat to be intensively abstracted from the bed without any danger that the contact mass may be extinguished, as well as permits concentrated sulphur dioxide to be processed without overheating the catalyst. For the same reason, it is no more necessary to preheat the gas to the catalyst ignition temperature.

Currently, fluidized-bed catalytic reactors are finding wide application in the industry. The laboratory setup simulates the work of the first bed of the contact mass in (a) a fluidized state of the catalyst and (b) a fixed catalyst bed.

This work is intended to determine the optimal conditions for contact oxidation of sulphur dioxide.

Experimental Setup and Procedure

The experimental setup for contact oxidation of sulphur dioxide is shown schematically in Fig. 43. To obtain a gas mixture containing

7 to 15% of SO_2, sulphur dioxide is fed from a bottle *6* through a drying bottle *4* with sulphuric acid and a rheometer *3* into a mixer *2*. The latter also receives air driven by an air blower (not shown) and freed of impurities and moisture with the aid of a charcoal filter *5* and bottles *4* with sulphuric acid. Its flow rate is measured by the rheometer *3*. The resulting gas mixture flows from the mixer into the catalytic reactor *1* in which sulphur dioxide is oxidized and from which the gas is vented into the atmosphere. The sulphur dioxide concentration before and after contacting is determined iodometrically
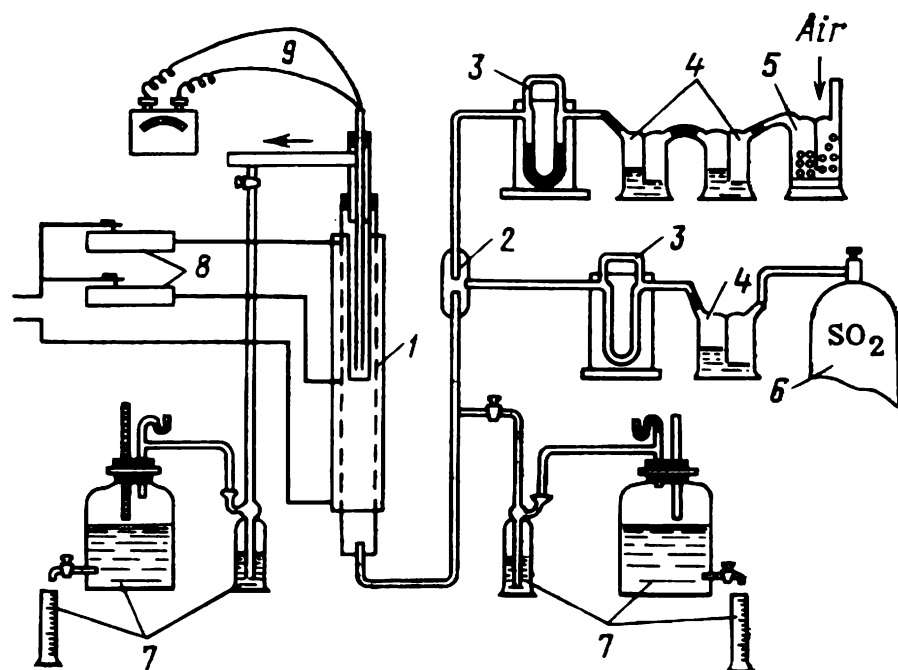
Fig. 43. Experimental setup for oxidation of sulphur dioxide in fluidized catalyst bed

with the aid of an analyzer *7*. The temperature in the catalytic reactor is measured by a chromel-alumel thermocouple connected to a galvanometer *9*. The heating of the reactor is controlled by means of rheostats *8*. The thermocouple is adapted to move freely within a porcelain jacket, which allows the temperature to be measured over the entire height of the catalyst bed. The tubular catalytic reactor is illustrated in Fig. 44.

When oxidation is conducted in a fluidized catalyst bed, a 10-mm high layer of crushed quartz is spread over the grid *5* of the reactor in the form of a quartz tube *1* (Fig. 44*a*) for a better gas distribution across the tube, on top of which a 30- to 50-mm high catalyst bed is placed. It is recommended to use a catalyst of the following granulometric composition: (a) particles from 0.25 to 0.5 mm in size and (b) particles from 0.5 to 1 mm in size. In this case, the gas mixture is supplied into the lower part of the reactor. The heating of the supplied gas mixture and the bed temperature are controlled by the main and auxiliary heating coils *2* and *3*, respectively. The

gas mixture is supplied at rates ranging from 2500 to 7500 cm³/min, which corresponds to space velocities of 5000 to 15 000 h⁻¹.

The reactor for oxidation of sulphur dioxide in a fixed catalyst bed (Fig. 44b) has three independently controlled heating coils 8, 9 and 10 for even distribution of the temperature in the bed. 15 to 20 cm³ of a catalyst with a grain size of 3 to 5 mm are charged into the annulus formed by the jacket of a thermocouple 11 [and quartz tube 13 provided with heat insulation 12 over the entire length of the heating coils. The gas is fed into the reactor from up [downward at rates ranging from 300 to 700 cm³/min, which corresponds to space velocities of 1000 to 2500 h⁻¹.

Before the experiment, the reactor is charged with a predetermined amount (by volume) of the catalyst of a particular average grain size. The reactor is then closed, and the heating [coils are energized. As soon as the temperature in the catalyst bed becomes as high as 120-150°C, the air blower is switched on, and the air flow rate is adjusted by means of the rheometer. The amount of the supplied air is controlled by a screw clamp, while the bed temperature is controlled by rheostats. The sulphur dioxide necessary for obtaining the gas mixture of a specified composition starts being fed at 400 to 450°C. Its flow rate is measured by a rheometer. The precise composition

Fig. 44. Catalytic reactor with fluidized (a) and fixed (b) beds

1, 13—quartz tube; *2, 3*—common and additional heating coils; *4*—heat insulation; *5*—grid; *6*—thermocouple tube; *7*—plugged tee; *8, 9, 10*—heating coils; *11*—thermocouple jacket; *12*—heat insulation

of the gas mixture supplied into the reactor is determined by analysis. The temperature in the reactor is maintained at 400 to 600°C depending on the experimental conditions.

After the degree of oxidation under given conditions has been determined, the sulphur dioxide supply is cut off, and the system is blown with air at 500°C till disappearance of the white mist of sulphur trioxide at the reactor exit. Then, the heating coils are de-energized, the air blower is switched off, and all valves in the inlet and outlet lines are closed.

Determination of the SO₂ Content in the Gas. The determination of sulphur dioxide by the recommended method is based on the reac-

tion of oxidation of SO_2 with iodine:

$$SO_2 + I_2 + H_2O \rightarrow H_2SO_4 + 2HI.$$
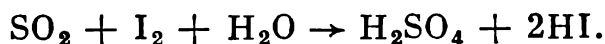
To determine the percentage content of sulphur dioxide in the initial gas, the gas mixture is analyzed upstream of the reactor. This is done by opening the valve and forcing the gas mixture through an absorption flask with an iodine solution by means of an aspirator.

Prior to analysis, 10 cm^3 of a 0.1 N iodine solution are poured into the flask, diluted with water to 50 cm^3, and 5 to 10 drops of starch are added. The gas is passed through the flask till the iodine solution loses colour. The water flowing out of the aspirator is collected into a measuring cylinder. The amount of this water corresponds to the volume of the passed gas, except for that of the sulphur dioxide absorbed in the flask with the iodine solution. The gas temperature in the aspirator is measured by a thermometer. The volume of the gas to be analyzed is equal to the volume of the gas sample in the aspirator, v_1, plus the volume of the sulphur dioxide, v_0, absorbed in 10 cm^3 of the 0.1 N iodine solution (reduced to the experimental conditions).

The gas is aspirated in such a manner that the pressure in the aspirator is at the atmospheric level, which is controlled by a water gauge. In this case, 10 cm^3 of the 0.1 N iodine solution correspond to 0.03 203 g of SO_2 which occupy, at 0°C and $1.01 \cdot 10^5$ Pa, a volume equal to 10.95 cm^3. For approximate determinations,

$$\%SO_2 = v^0 100/(v_1 + v_0) = 1095/(10.95 + v_1). \qquad (2.25)$$

In practice, use is often made of a table permitting the percentage content of sulphur dioxide to be determined from the amount of the water that has flowed out of the aspirator (see below). To precisely determine the percentage content of sulphur dioxide in the analysis, its volume must be reduced to normal conditions. For this purpose, it is convenient to use Table 7 in which the volume of sulphur dioxide, absorbed in 10 cm^3 of the 0.1 N iodine solution, has been calculated for different temperatures and pressures from the formula

$$v_{p,\,t} = \frac{v_0\,(273+t)\,1.01\cdot10^5}{273\,(P-p)}, \qquad (2.26)$$

where $v_0 = 10.95$ cm^3; t is the gas temperature in the aspirator; P is the atmospheric pressure; and p is the water vapour pressure, in Pa.

Then,

$$\%SO_2 = v_{p,t}100/(v_1 + v_{p,t}). \qquad (2.27)$$

The percentage content of sulphur dioxide after contacting is determined in a similar manner. In this case, the absorption flask

Table 7

Water vol- ume, cm³	SO₂ content, %			
	in 10 cm³ of 0.1 N I_2 solution		in 10 cm³ of 0.01 N I_2 solution	
	15 °C	20 °C	15 °C	20 °C
100	10.3	10.5	1.14	1.15
110	9.5	9.6	1.03	1.05
120	8.8	8.9	0.95	0.97
130	8.2	8.3	0.88	0.89
140	7.6	7.7	0.81	0.83
150	7.1	7.2	0.76	0.77
160	6.7	6.8	0.71	0.73
170	6.4	6.5	0.67	0.69
180	7.0	6.1	0.64	0.65
190	5.7	5.8	0.60	0.61
200	5.5	5.6	0.57	0.58

is filled with 10 cm³ of a 0.01 N iodine solution. The degree of oxi- dation x of sulphur dioxide (SO_3 yield) is expressed in per cent:

$$x = \frac{(C_1 - C_2)\,100}{C_1} \cdot \frac{100}{100 - 1.5 C_2}, \qquad (2.28)$$

where the factor $100/(100 - 1.5 C_2)$ takes into account the decrease in the mixture volume as a result of the reaction. Approximate estimations can be based on the formula

$$x = (C_1 - C_2)\,100/C_1, \qquad (2.29)$$

where C_1 and C_2 stand for the sulphur dioxide concentrations in the starting and oxidized gas, respectively.

In a more detailed study of the process in the fluidized bed, assum- ing perfect mixing of the reaction medium, the reaction rate constant can be calculated using Eq. (2.23) in a transformed form:

$$k = \frac{2ax}{\tau} \left(\frac{x}{x_{eq} - x)} \right)^{0.8} \frac{1}{2b - ax} \cdot \frac{T}{273} \beta, \qquad (2.30)$$

where $\tau = v_{cat}/V$ is the theoretical time of contact between the gas and catalyst at 0°C and $1.01 \cdot 10^5$ Pa, in s; v_{cat} is the catalyst volume, in m³; V is the gas mixture volume, in m³/s; a and b are determined by analysis of the gas upstream of the reactor; and β is defined by the formula

$$\beta = \left(1 - x \frac{a}{2 \cdot 100} \right)^{-1}. \qquad (2.31)$$

The experimental and calculation results are summarized in the following table:

Catalyst volume, cm³	Space velocity		Contact time, s	Temperature in the reaction zone, °C	Analysis of the gas mixture				Degree of oxidation, %	Rate constant, s⁻¹
					upstream of the reactor		downstream of the reactor			
	SO₂	air			amount of water from the aspirator, cm³	SO₂, %	amount of water from the aspirator, cm³	SO₂, %		

The experimental data are presented as a plot of degree of oxidation x versus temperature T. If the temperature is varied at a constant amount of the catalyst and a constant flow rate of the gas in a definite concentration, the curve of Fig. 2 will be derived. And if the catalyst amount or gas flow rate are varied, a series of curves as shown in Fig. 36 will result, and a curve of optimal temperatures can be plotted. The experimental procedure can be verified approximately using Eq. (2.1) or (2.24).

The log k versus $1/T$ curve is used to determine the activation energy E for the catalyst under examination. According to the Arrhenius equation, the activation energy will vary directly with the slope of the experimental line toward the abscissa α (see Fig. 21):

$$E = 2.3R \tan \alpha. \tag{2.32}$$

LITERATURE

Amelin, A. G., *The Technology of Sulphuric Acid*, Moscow, 1971.

Mukhlyonov, I. P., Anokhin, V. N., *et al.*, *Catalysis in a Fluidized Bed*, Leningrad, 1978, pp. 117-131.

A Handbook for Sulphuric Acid Specialists, 2nd revised and expanded edition, Moscow, 1971, p. 744.

Instructions to the Laboratory Work
"Contact Oxidation of Sulphur Dioxide"

1. Load the catalyst into the reactor.
2. Close the reactor and energize the heating coils.
3. Switch on the air blower when the bed temperature reaches 120 to 150°C; adjust the air flow rate.
4. As soon as the temperature in the catalyst bed reaches 400 to 450°C, start feeding sulphur dioxide taking all the necessary precautions in handling the gas bottles; measure the sulphur dioxide flow rate by a rheometer. Make sure that the experimental setup is airtight and that sulphur dioxide does not leak out.
5. Analyze iodometrically the gas mixture fed into the reactor.
6. Maintain the temperature in the reactor at 400 to 600°C depending on the assignment.

7. After the experiment, cut off the sulphur dioxide supply from the bottle and blow the system with air for an hour at 400 to 500°C (till the white mist of sulphur trioxide at the reactor exit disappears).

8. De-energize the heating coils and switch off the air blower.

9. Close all the valves in the inlet and outlet lines.

10. Discharge the catalyst, if necessary, after the reactor has cooled completely.

LABORATORY WORK 14. OXIDATION OF AMMONIA

The oxidation of ammonia to nitrogen monoxide is the first step in the production of weak nitric acid, the second step being oxidation of nitrogen monoxide to nitrogen dioxide plus absorption of NO_2 in water. The oxidation of ammonia to nitrogen monoxide can be written using the following overall equation:

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 907.0 \text{ kJ} \tag{a}$$
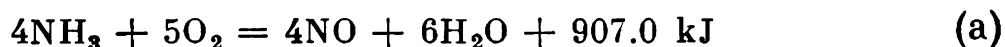
In addition to this main reaction, the oxidation of ammonia may involve the following side reactions:

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O + 1105.0 \text{ kJ} \tag{b}$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O + 1909.0 \text{ kJ} \tag{c}$$
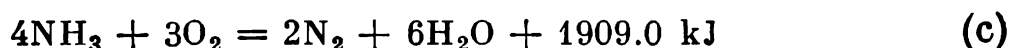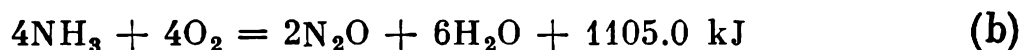
The equilibrium of these three exothermic reactions is shifted to the right, which follows from the values of the equilibrium constants of reactions (a) and (b) K_1 and K_2 at 500 and 1000°C, given in Table 8. Since the oxidation of ammonia is practically irreversible, its course is governed by the ratio of the rates of reactions (a) through (c), hence, by the process conditions determining the kinetics of these reactions.

Table 8

Constants	Temperature, °C	
	500	1000
$K_1 = \dfrac{p_{NH_3}^4 \, p_{O_2}^5}{p_{NO}^4 \, p_{H_2O}^6}$	10^{-75}	10^{-51}
$K_2 = \dfrac{p_{NH_3}^4 \, p_{O_2}^3}{p_{N_2}^2 \, p_{H_2O}^6}$	10^{-95}	10^{-62}

In the absence of a catalyst, the oxidation of ammonia proceeds, mainly, as in (c). Apart from reaction (c), molecular nitrogen may form in side processes occurring practically beyond the catalyst zone. If the temperature of the gas mixture is exceedingly high, dissociation of ammonia may take place before the mixture comes in contact

with the catalyst, accelerated catalytically under the effect of the reactor walls, according to the equation

$$2NH_3 = N_2 + 3H_2 \qquad\qquad (d)$$

Another side process involves dissociation of nitrogen monoxide in the following manner:

$$2NO = N_2 + O_2 \qquad\qquad (e)$$

The rate of reaction (e) is extremely low at a temperature below 1000°C. Finally, a reaction may take place between the resulting nitrogen monoxide and the unreacted ammonia:

$$4NH_3 + 6NO = 5N_2 + 6H_2O \qquad\qquad (f)$$

Reaction (f) seems to be the main cause of nitrogen defixation during catalytic oxidation of ammonia.

Practical implementation of the ammonia oxidation process calls for optimal conditions under which the yield of nitrogen monoxide in reaction (a) is maximum, while the amount of ammonia lost in the form of molecular nitrogen is minimum. To achieve such conditions, ammonia is oxidized in the presence of a highly active selective catalyst, within a relatively narrow temperature range, at strictly controlled timing of gas contact with the catalyst (contact time) and initial composition of the ammonia-air mixture. The catalyst must selectively speed up the main reaction of oxidation of ammonia to nitrogen monoxide, without affecting the rates of other thermodynamically possible reactions (b) and (c). The most widely used commercial catalyst of ammonia oxidation is platinum or its alloys with palladium and rhodium. Various alloys of platinum and palladium with added amounts of rhodium, silver, cobalt, iridium, and other metals ensure a high yield of nitrogen monoxide (96-98%) within a short contact time. It takes virtually ten-thousandths of a second for ammonia to oxidize completely to nitrogen monoxide. The catalyst retains its activity for a long period of time. However, the high cost of platinum and the inevitable loss (entrainment) of this metal necessitate the use of other cheaper materials; employed at present apart from platinum are catalysts based on iron or cobalt oxides, activated by addition of chromium, manganese, and bismuth. Many of the oxide catalysts have displayed high activity (ensuring a nitrogen monoxide yield of up to 94%), however, it tends to wane in the course of time.

Raising temperature enhances the yield of NO by virtue of reaction (a) being accelerated to a certain limit. The maximum yield of nitrogen oxide (95-98%) over a platinum catalyst is attained at 800°C and $P = 1.01 \cdot 10^5$ Pa as well as at 900°C and $P = 11 \cdot 10^5$ Pa. If the temperature is increased further, the yield of NO is reduced by side reactions (d) and (f) in which elementary nitrogen is formed and greater amounts of platinum are lost.

The yield of nitrogen monoxide varies markedly with the composition of the starting gas mixture. Theoretically, 1.25 moles of oxygen are required for oxidation of one mole of NH_3 to NO. For a higher yield of NO, oxygen must be in excess of the theoretical amount. According to experimental data, in commercial production a high yield of NO can be achieved if the volumes of oxygen and ammonia are at a ratio of at least 1.8-2.0 to 1, respectively. This ratio must be maintained at an initial ammonia concentration in the ammonia-air mixture of 9 to 9.5%. To obtain more concentrated nitrous gases (which promotes the subsequent processes of oxidation and absorption of nitrogen oxides), the content of ammonia in the initial gas is increased and air is enriched with oxygen in order to maintain the necessary ratio of NH_3 and O_2 volumes. However, the explosive nature of ammonia-air mixtures imposes a limitation on the extent to which the ammonia concentration in the gas may be increased. The reaction of oxidation of ammonia to nitrogen monoxide proceeds in the external diffusion region both over platinum and oxide catalysts. The time τ of contact between the gas and catalyst can be defined using the equation

$$\tau = v_f/V_g, \qquad (2.33)$$

where v_f is the free volume of the catalyst (volume of voids in meshes or between grains), in m^3, and V_g is the volume velocity of the gas under process conditions, in m^3/s.

The contact time can also be determined from the kinetic equation of the ammonia oxidation reaction

$$-dp_{NH_3}/d\tau = kp_{NH_3}. \qquad (2.34)$$

As can be inferred from Eq. (2.34), the ammonia oxidation rate is determined by the slowest limiting step of the process, that is diffusion of ammonia toward the catalyst surface. In accordance with Eq. (2.34),

$$\tau = \frac{1}{k}\ln\frac{1}{1-x}, \qquad (2.35)$$

where k is the process rate constant, in s^{-1}; τ is the contact time, in s; and x is the percentage conversion of NH_3.

The optimal contact time is 10^{-4} to 10^{-5} s over platinum catalysts and about 10^{-2} s over oxide catalysts.

The aim of this work is the study of the catalytic oxidation of ammonia and ways to control this process, using a laboratory model plant, and, more specifically, the determination of the dependence of the contacting ratio (yield) on the temperature in the contact zone and oxidation time (time of residence of the gas in the contact zone).

Experimental Setup and Procedure

The continuous system for oxidation of ammonia is shown sche-
matically in Fig. 45. The catalytic reactor used in the system is es-
sentially a quartz tube with a catalyst, accommodated in a vertical
electrically heated tube furnace. The temperature inside the reactor
is measured and controlled by an automatic device (pyrometric con-
trol millivoltmeter). The quartz tube contains a non-platinum (e.g.
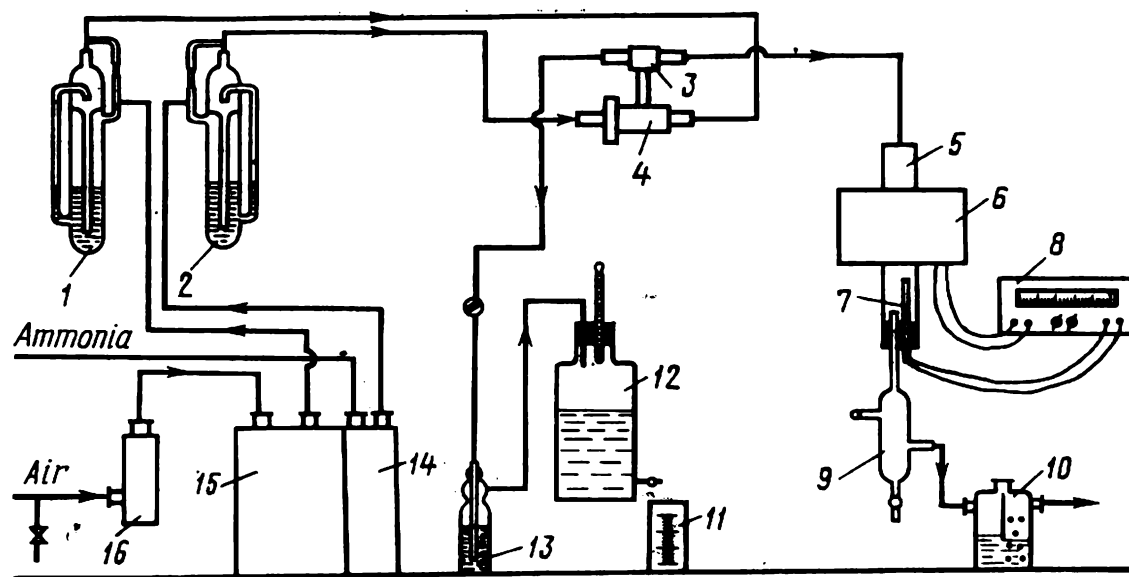
Fig. 45. Experimental setup for oxidation of ammonia

6, 2—rheometer; *3*—three-way valve; *4*—mixer; *5*—reactor (quartz tube with catalyst);
1—tube furnace; *7*—thermocouple; *8*—automatic temperature controller; *9*—gas sampler;
10—absorption bottle; *11*—measuring cylinder; *12*—aspirator; *13*—Drexel bottle; *14, 15*—
quffer vessel; *16*—oil separator

iron oxide or cobalt) granulated catalyst or a stack of several pla-
tinum meshes. The tube is about 300 mm long and 20 to 30 mm in
diameter. In the lower part of the tube is placed a quartz layer top-
ped by a bed of catalyst granules, 60 to 80 mm in height, so that
the latter occupies the middle heated part of the furnace. In the
lower part of the catalyst-containing tube is arranged a holder for
a thermocouple having its end in the centre of the tube. The gas is
fed into the reactor from the top through a glass tube and leaves the
reactor through a gas discharge tube at its bottom. The gas discharge
tube is thermally insulated by an asbestos cord. The quartz tube
for platinum catalyst must have projections on its inner wall, on
which platinum meshes are arranged one on top of another. The up-
per mesh is pressed against the support, that is the respective pro-
jections, by a quartz ring.

The gas mixture is prepared as follows: ammonia from a bottle
is fed through a buffer vessel *14* and a rheometer into a glass or alu-
minium mixer in which it is mixed with the air driven in by an air

blower via another buffer vessel *15* and a rheometer. An oil separator, which is essentially a vessel filled with ceramic beads, is inserted between the air blower and buffer vessel *15*. The oil separator, vessels, and mixer are made of glass or aluminium. The gas is delivered from the mixer into the catalytic reactor from up downward. For absorption of nitrogen oxides, the gas downstream of the reactor is driven through an absorption flask with a sodium hydrate solution into an exhaust hood. To sample the ammonia-air mixture for analysis, provision is made for a three-way valve through which the gas flows into a Drexel bottle and is collected in an aspirator; the gas downstream of the reactor is sampled for analysis with the aid of a gas sampling tube.

Before the experiment, the flow rates of the ammonia and air, required to prepare a gas mixture containing 8 to 9% of NH_3, are adjusted by means of precalibrated rheometers. The overall volume velocity of the gas mixture must range from 200 to 1000 cm^3/min (12 to 60 dm^3/h). The composition of the gas is established precisely and controlled by analysis. The gas mixture is fed at a definite rate into the catalytic reactor heated to the desired temperature (600 to 850°C). During the experiment, the gas flow rate and temperature in the reactor are maintained constant. Every 10 minutes in the course of the experiment, parallel gas samples are taken two or three times before contacting, to determine the NH_3 content, and also downstream of the reactor, to determine the content of nitrogen oxides. The same sequence is followed when experiments are conducted under a different set of conditions. The variable parameters may include the composition of the initial gas (the amount of ammonia it contains), temperature, and contact time. When one of the process parameters is changed, the rest of them must remain constant.

The results of analyses are used to calculate the degree of oxidation under each set of conditions, average data being taken from several parallel analyses carried out under the same conditions. Curves representing the degree of oxidation versus temparature or contact time are plotted from the experimental results, and the optimal conditions of the process are defined within a particular range of process parameters. The contact time τ is calculated using Eq. (2.33).

Since the free volume of a particular catalyst is a constant quantity, it is more common to determine the so-called theoretical contact time τ_{th} from the total catalyst volume v_{cat}:

$$\tau_{th} = v_{cat}/V_g,$$

where V_g is the volume velocity of the gas, in cm^3/s, and v_{cat} is the volume occupied by the catalyst, in cm^3.

As a measure of catalyst activity the conversion (contacting) ratio x is used which is defined for this irreversible process as the ratio of the amount of ammonia oxidized to nitrogen monoxide to

the initial quantity of ammonia in the gas, in accordance with the formula

$$x = (C_2/C_1)\ 100,$$

where C_1 is the ammonia content in the initial gas, in % by weight, and C_2, is the NO content, in terms of NH_3, in the gas after contacting, in % by weight.

Analytical and Data Processing Procedures

The starting gas mixture is analyzed for NH_3 content by passing the gas with the aid of the aspirator and valve (see Fig. 45) through the absorption Drexel bottle which has been filled with 50 cm³ of water, 10 cm³ of 0.1 N HCl, and several drops of methyl orange. The absorption bottle communicates with the aspirator creating a negative pressure for the gas to be driven through the absorption bottle. The gas is let through the latter till the solution changes its colouration from red to yellow. The amount of the air in the ammonia-air mixture sampled for analysis is determined from the volume of the water that has flowed out of the aspirator.
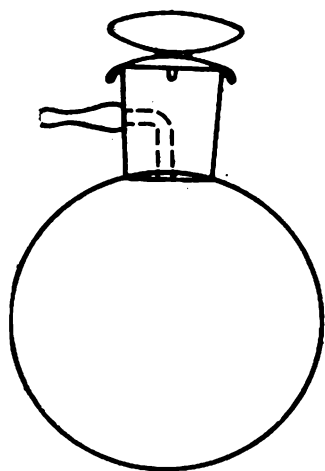
The ammonia content C' in the gas (vol. %) is calculated using the formula

$$C' = a100 \cdot \left(\frac{v273\,(P-p)}{(273+t)\,1.01 \cdot 10^5}\right)^{-1},$$

Fig. 46. Flask for gas analysis after contacting

where a is the volume of NH_3 (10 cm³ of 0.1 N HCl corresponds to 22.4 cm³ of NH_3 at 0°C and $1.01 \cdot 10^5$ Pa), in cm³; v is the volume of the water from the aspirator, in cm³; P is the barometric pressure, in Pa; t is the ambient temperature, °C; and p is the partial pressure of water vapours at temperature t, in Pa.

The *analysis of gas after contacting* is carried out by the evacuated flask method. A round-bottomed flask (Fig. 46) is charged with 5 cm³ of 3% hydrogen peroxide solution, then, after the flask has been put into a cloth bag (or wrapped in a towel), it is connected to a vacuum pump by a rubber hose; air is pumped off the flask till the residual pressure in it is 26 600 to 39 900 Pa. After that, the ground-glass joint of the flask is tested for air-tightness; to this end, the flask is turned upside down, to see whether air gets inside (if the flask is not airtight, air bubbles passing through the hydrogen peroxide solution become visible). If the ground-glass joint of the flask is not airtight, the stopper must be removed, the neck of the flask must be wiped dry with filter paper and receive a coat of vacuum grease,

the stopper must be lapped against the neck, the flask must be re-closed and evacuated again.

The flask is weighed on an analytical balance, and the gas mixture to be analyzed is sucked into it after the flask has been connected to the gas sampling tube (see Fig. 45). Before sampling, the condensate is drained, and the drain outlet of the gas sampling tube is blown with the gas to be analyzed. The gas is sampled into the flask carefully by turning the glass-ground stopper till its perforations are aligned with the opening in the gas sampling appendage of the flask neck. As the stopper is being turned, the liquid level in the gauge is observed, the gas sampling opening being closed and reopened to avoid a surge of the liquid in the rheometer. The gas sampling is carried on till the liquid in the gauge stops fluctuating (surging), that is till the pressure inside and outside the flask is equalized. After the sample has been taken, the flask with the gas is weighed once more, and the amount of the gas is determined from the weight difference. The flask is then shaken for 15 to 20 minutes on a shaker. At the same time, the oxygen of the air inside the flask and hydrogen peroxide oxidize nitrogen oxides to nitric acid which is then titrated with a sodium hydrate solution. For this purpose, the contents of the evacuated flask are decanted into a conical one to which are added the washes resulting from the flask being rinsed with several portions of distilled water.

Prior to titration, the excess hydrogen peroxide must be decomposed by boiling for a short period of time after a measured amount of 0.1 N NaOH has been added to the solution under analysis. The alkali is taken in an excess amount specified by the instructor depending on the concentration of nitrogen oxides in the gas. The excess amount of sodium hydrate is titrated, after the 0.1 N HCl solution has been boiled and cooled, in the presence of methyl orange. The amount of the alkali spent to neutralize the nitric acid is recalculated with respect to oxidized ammonia using the formula

$$C_2 = (a - b)\ 0.0017 \cdot 100/G, \qquad (2.36)$$

where C_2 is the content of oxidized ammonia in the final gas, in % by weight; a is the amount of 0.1 N NaOH added to the analyzed solution, in cm^3; b is the amount of 0.1 N HCl spent in the titration of excess NaOH, in cm^3; $(a - b)\ 0.0017$ is the amount of ammonia oxidized to NO in the gas sample, in g; and G is the sample weight, in g.

To determine the degree of oxidation, the ammonia content in the initial gas is also calculated in terms of per cent by weight according to the formula

$$C_1 = \frac{C' 17 \cdot 100}{C' 17 + (100 - C')\ 28}, \qquad (2.37)$$

where C' is the NH_3 concentration, in % by volume; C_1 is the NH_3 concentration, in % by weight; 17 and 28 stand, respectively, for the molecular weights of ammonia and air.

The results of experiments and calculations should be tabulated as follows:

Temperature in contacting zone t, °C	Volume velocity of, cm³/min			Catalyst volume v, cm³	Contact time τ, s	NH₃ content in initial gas		Content of oxidized NH₃ in contact gas C_2, wt. %	Contacting ratio x, %
	ammonia	air	ammonia-air mixture			C', vol. %	C_1, wt. %		

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Atroshchenko, V. I. and Kargin, S. I., *The Technology of Nitric Acid*, 3rd revised and expanded edition, Moscow, 1970.

Instructions to the Laboratory Work "Oxidation of Ammonia"

1. Switch on the heating of the catalytic reactor.

2. Switch on the air blower with its three-way valve being fully open into the atmosphere.

3. Preset the air flow rate by the screw clamp of the air blower's three-way valve.

4. When preparing the ammonia-air mixture, feed air into the system first, then, after the preset air flow rate has been attained, start feeding ammonia.

5. When feeding ammonia, do not exceed the predetermined flow rate so that the amount of ammonia in the mixture is not greater than 9%, to avoid formation of explosive ammonia-air mixtures.

6. By carefully and gradually opening the ammonia bottle, adjust the ammonia flow rate using an ammonia rheometer.

7. Determine by analysis the composition of the initial gas mixture and adjust it, if necessary, in accordance with the assignment.

8. Prepare an evacuated flask (which must be in a cloth bag) for analysis of nitrous gases and weigh it on an analytical balance. The residual pressure in the evacuated flask must be at least $40 \cdot 10^3$ Pa.

9. Maintain the prescribed temperature in the catalytic reactor for at least 15 minutes.

10. Sample the nitrous gases (downstream of the reactor) into the evacuated flask and, at the same time, check analytically the composition of the initial gas.

11. Calculate the contacting ratio at a given temperature from the results of analysis of the initial ammonia-gas mixture and nitrous gases downstream of the reactor.

LABORATORY WORK 15. DEHYDROGENATION OF ETHYL BENZENE

The dehydrogenation of ethyl benzene, yielding styrene and its homologues widely used in the production of synthetic rubbers and plastics, is conducted over various solid catalysts containing ZnO, Cr_2O_3, Al_2O_3, and other oxides:

$$C_6H_5 - CH_2 - CH_3 \longrightarrow C_6H_5 - CH = CH_2 + H_2 - Q$$

The dehydrogenation reaction, in which the C—C bonds in the alkyl group are activated, may be accompanied by reactions, in which the C—C bonds are split; in this case, saturated, unsaturated, and aromatic hydrocarbons are formed as a consequence of hydrogen removal during the dehydrogenation. Heating of ethyl benzene to 600°C may cause the following reactions on solid catalysts:

$$C_6H_5 - CH_2 - CH_3 \rightarrow C_6H_5CH = CH_2 + H_2 \qquad \text{(a)}$$

$$C_6H_5 - CH_2 - CH_3 \xrightarrow{H_2} C_6H_5 - CH_3 + CH_4 \qquad \text{(b)}$$

$$C_6H_5 - CH_2 - CH_3 \xrightarrow{H_2} C_6H_6 + C_2H_6 \qquad \text{(c)}$$

$$C_6H_5 - CH_2 - CH_3 \rightarrow C_6H_6 + C_2H_4 + 1/2H_2 \qquad \text{(d)}$$

$$C_6H_5 - CH_2 - CH_3 \xrightarrow{H_2} C_6H_6 + 2CH_4 \qquad \text{(e)}$$
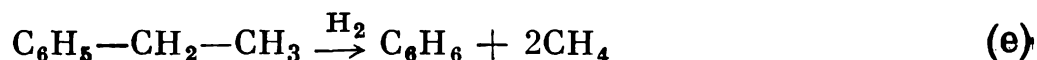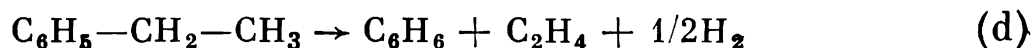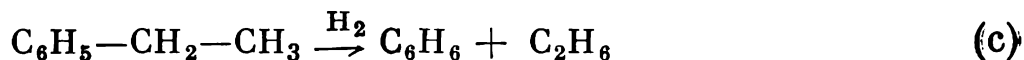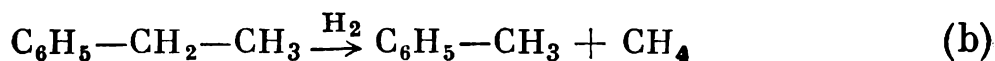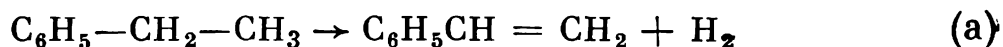
The dehydrogenation of ethyl benzene is a reaction yielding products in an amount greater than that of the starting reagent (in the vaporous state). Therefore, by decreasing pressure one can enhance the yield of styrene. Instead of negative pressure which is technically difficult to attain at elevated temperatures, one can reduce the partial pressure of ethyl benzene by feeding steam into the reaction zone. For example, if at a pressure of $1.01 \cdot 10^5$ Pa the equilibrium yield of styrene is 25 to 30% at 630°C, dilution with steam shifts the equilibrium and increases the styrene yield up to 70-80%. Table 9 lists the equilibrium conversion ratios of ethyl benzene for various temperatures at different degrees of dilution with steam.

Table 9

Temperature, °C	Equilibrium conversion ratio at dilution with steam		
	$n^* = 0$	$n = 16$	$n = 20$
520	18	54	57
560	29	70	75
600	41	82	85
620	55	90	91

* n is the number of moles of steam per mole of ethyl benzene.

Steam is fed into the system in an amount of 1.2 to 2.6 kg per kg of ethyl benzene, depending of the catalyst type and process conditions. With the aid of steam one can also control the temperature in the reaction zone; besides, steam can be used as a catalyst regenerating agent interacting in the reaction zone with the carbon released as a result of side reactions and yielding carbon monoxide, carbon dioxide, and hydrogen. The product yield increases with temperature as a consequence of the endothermic nature of the reaction (see Fig. 3). However, when the temperature is raised, the increase in the reaction rate is accompanied by thermal decomposition of ethyl benzene, and formation of benzene and toluene. Depending on the catalyst type and composition, the optimal process temperatures ensuring a sufficiently high reaction rate and a minimal amount of by-products range from 560 to 650°C.

The catalysts of ethyl benzene dehydrogenation in most cases contain a single compound (metal oxide) as the main component plus small amounts of other components. Catalysts remaining active over a long period of time without being deactivated by steam include contacts of the following composition: ZnO—50%, Al_2O_3—40%, and CaO—10%; after a year of the catalyst operation, the yield of styrene at 650°C is 75%, whereas over a fresh catalyst, the yield is 85%. The catalyst of the following composition: ZnO—86%, Al_2O_3—4%, CaO—5%, K_2CrO_4—3%, and K_2SO_4—2%, works optimally at temperatures ranging from 580 to 620°C without a perceptible change in its activity for one and half years, ensuring a 90% yield of styrene. By slightly altering the composition of this catalyst (ZnO—82%, Al_2O_3—8%, and CaO—5%) and adding 3% of K_2CrO_4 and 3% of K_2SO_4, one can lower the optimal temperature range to 560-570°C bringing the styrene yield up to 93%. The presence of potassium oxide in the contact promotes the interaction of the carbon, released in the reaction zone, with steam.

The process is conducted in polythermal industrial tubular reactors. Flowing through the tube space is a gaseous heat-transfer agent, while the catalyst is inside the tubes.

In this work, styrene must be produced by catalytic dehydrogenation of ethyl benzene with determination of its yield depending on the catalyst type, contact time, process temperature, and composition of the starting gas mixture to be diluted with steam.

Experimental Setup and Procedure

Figure 47 shows schematically the experimental setup for dehydrogenation of ethyl benzene. Used as the reactor *6* is a porcelain or quartz tube placed in a horizontal electrically heated tube furnace *4*. The catalyst *5* is placed into the reactor tube. Ethyl benzene and water are fed into the reaction zone by a metering device *3* (dispens-

er, microburette, dropping funnel). When the process involves addition of water, it is preferable to employ a quartz reactor because porcelain tubes are less resistant to temperature stresses. The temperature in the reaction zone is registered and controlled by the thermocouple *2* of an automatic recorder *1*.

The gas mixture emerging from the reactor furnace passes through a condenser *7*, and the high-boiling fractions (including styrene and unreacted ethyl benzene) are condensed and collected in a receiver *8*.
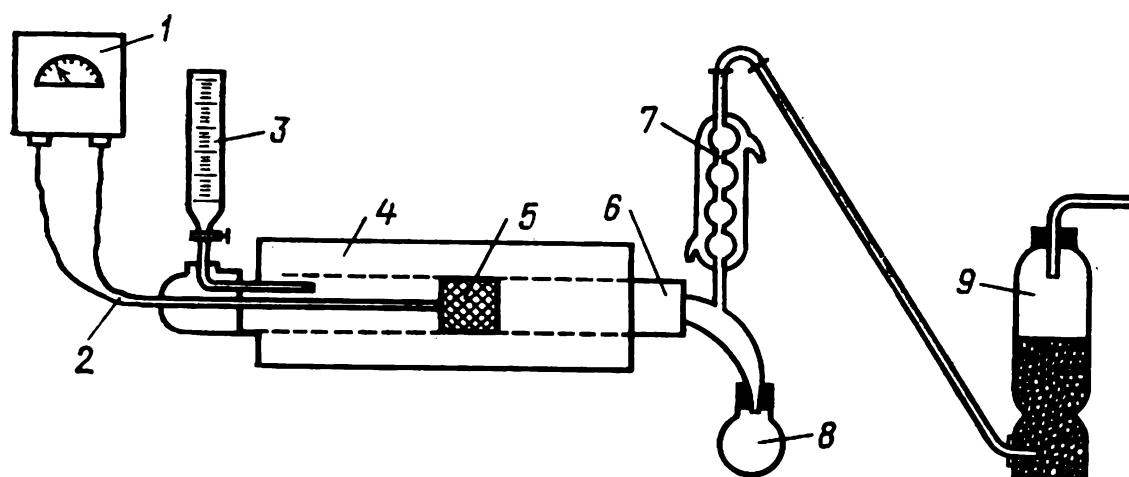
Fig. 47. Experimental setup for dehydrogenation of ethyl benzene

The uncondensed reaction products go into an adsorption vessel *9* filled with activated charcoal. The gas is driven through the system by a water-jet pump connected to the discharge pipe of the adsorption vessel *9*.

The reactor is charged with an appropriate catalyst taken in an amount of 10 to 40 cm³ according to the assignment, and then placed into the furnace. The system is put together as shown, ethyl benzene and water are poured into the metering device, the temperature controller is preset to the desired temperature, and the heating coils of the furnace are energized. As soon as the prescribed temperature is reached, the water-jet pump is switched on, and water is supplied into condenser *7*. Ethyl benzene is fed at a rate of 1 g/min per 100 cm³ of the catalyst. If the process is conducted with steam, distilled water is also fed at a preset rate simultaneously with ethyl benzene. When the experiment is over, receiver *8* is disconnected, and the condensate is weighed to determine the styrene yield as percentage of the theoretical. The styrene content in the condensate is determined by bromination of the unsaturated bond:

$$C_6H_5CH = CH_2 + Br_2 \rightarrow C_6H_5CHBr - BrCH_2$$
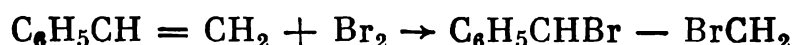
To this end, 0.2 to 0.25 g (8 to 10 drops) of the condensate are transferred into a flask with a glass-ground stopper, having a capacity of 250 to 300 cm³, 30 to 35 cm³ of an 0.1 N titrated bromine solution

are added from a burette, the flask is stoppered, shaken and allowed to stand for 5 to 10 minutes; this is followed by addition of 10 to 15 cm³ of a 10% solution of KI and the same amount of water. After 10 minutes the mixture is carefully stirred to titrate the liberated iodine with 0.1 N Na₂S₂O₃ in the presence of starch used as an indicator. The content of styrene in the condensate (wt. %) is calculated using the equation

$$x = \frac{(m-n)\, 0.0052 \cdot 100}{g},$$

where m is the amount of titrated 0.1 N Br₂, in cm³; n is the amount of 0.1 N Na₂S₂O₃ spent in the titration of the excess reagent, in cm³; g is the weighed amount of the condensate, in g; and 0.052 is the amount of styrene corresponding to 1 cm³ of 0.1 N Na₂S₂O₃.

The styrene yield y (percentage of the theoretical) is

$$y = G_c x 106/A 104,$$

where G_c is the weight of the condensate, in g; x is the styrene content in the condensate, in %; A is the weight of the initial ethyl benzene, in g; 106 and 104 stand, respectively, for the molecular weights of ethyl benzene and styrene.

The experimental results must be entered in the following table:

Catalyst volume, cm3	Ethyl benzene volume, cm3	$\dfrac{C_6H_5-C_2H_5}{H_2O}$	Temperature in the reaction zone, °C	Condensate weight, g	Styrene content in the condensate, wt. %	Styrene yield, %

The catalysts for dehydrogenation of ethyl benzene are prepared by blending solid metal oxides, for example, Cr_2O_3 or Al_2O_3, with solutions of salts, such as $Mg(NO_3)_2$ or $Zn(C_2H_3O_2)_2$. The starting materials used in the preparation of dehydrogenation catalysts may include the following substances: (1) $Mg(NO_3)_2 + MgO + Cr_2O_3$; (2) $MgO + (NH_4)_2Cr_2O_7$; (3) $Zn(NO_3)_2 + Al_2O_3$; (4) $Zn(C_2H_3O_2)_2 + + Al_2O_3$; (5) $Zn(NO_3)_2 + Al_2O_3$.

For example, to prepare 100 g of the magnesium-chromium catalyst, 10 g of $Mg(NO_3)_2$ are dissolved in 60 cm³ of water and mixed with 80 g of MgO and 10 g of Cr_2O_3. The resulting paste is granulated by extrusion or through a perforated metal plate, dried at 100 to 110 °C, and baked at 350 to 400 °C for 4 to 5 hours. The mixture can be dried and baked without preliminary granulation, with subsequent crushing and separation on a sieve of the dust and fine particles to obtain grains of the right size. From 2 to 4% of starch may be

added during blending, as a binder and pore forming agent. The component ratios may be varied. Zinc-aluminium catalysts are prepared in a similar fashion.

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Litvin, O. B., *The Basic Technology of Rubber Synthesis*, 3rd revised and expanded edition, Moscow, 1972.

Instructions to the Laboratory Work "Dehydrogenation of Ethyl Benzene"

1. Charge the necessary amount of the catalyst into the reactor.
2. Before the experiment, make sure that the system has been properly assembled, and test it for air-tightness connecting an aspirator to the adsorption vessel.
3. Switch on the furnace and start feeding ethyl benzene after the prescribed temperature has been reached.
4. Do not switch on the water-jet pump with the burette stopcock closed, that is do not create vacuum in the furnace.
5. Ethyl benzene is highly inflammable. If it catches fire outside the furnace, put out the flame by sand or (if the flame is intense) by a fire extinguisher.
6. Do not overheat the furnace above 650°C by maintaining the temperature within the specified limits in accordance with the catalyst used.
7. After the last drops of ethyl benzene have left the burette, close the burette stopcock for not more than 5 minutes. Then, reopen the stopcock with air being blown into the furnace and switch off the water-jet pump.
8. After the dehydrogenation is over, determine the styrene content in the condensate by bromination.
9. Handle the bromine water under an exhaust hood (see the general instructions concerning the safety precautions in the laboratory, Section "Toxic Substances").

LABORATORY WORK 16. CATALYTIC DEHYDROGENATION OF ALKYL BENZENES

The basic theory of catalytic dehydrogenation of alkyl benzenes (ethyl benzene) and catalysts have already been described in Work 15. The purpose of this work is to study separate and combined catalytic dehydrogenation of alkyl benzenes using a large-scale laboratory setup with chromatographic analysis of the starting substances and reaction products, as well as calculation of the basic process parameters.

Experimental Setup and Procedure

The setup, shown schematically in Fig. 48, comprises the following main sections: stock metering, catalytic reactor, condensation and separation, and thermal.
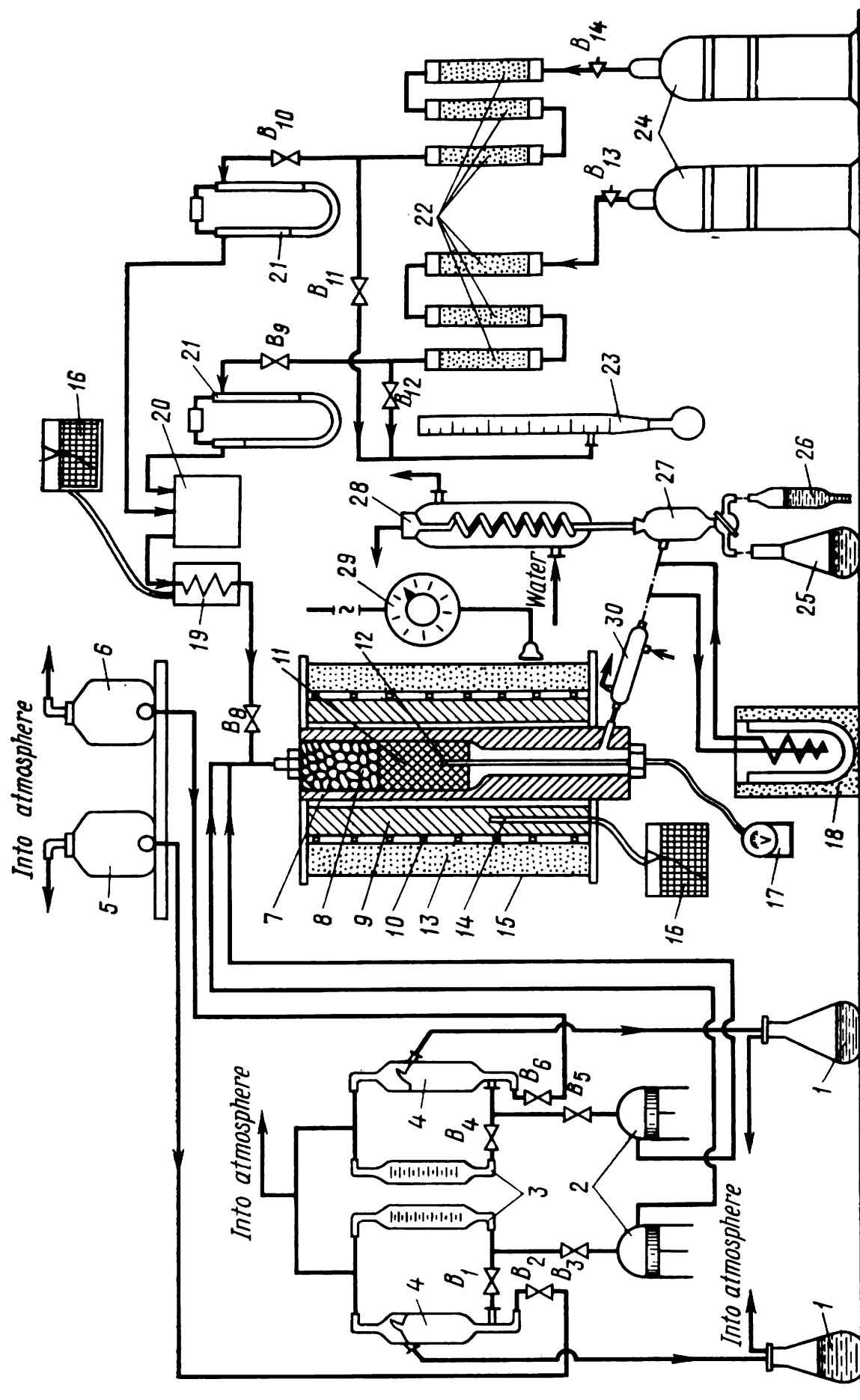
Fig. 48. Large-scale experimental setup dehydrogenation of alkyl benzenes

1, 25—collector; 2—micropump; 3—burette; 4—intermediate vessel; 5—alkyl benzene vessel; 6—diluent bottle; 7—reactor; 8—vaporizer; 9—resistance furnace; 10—heating element; 11—contact zone; 12, 14—thermocouple; 13—insulation; 15—furnace casing; 16—recorder; 17—portable potentiometer; 18, 19—preheater; 20—mixer; 21—rheometer; 22—gas cleaning tube; 23—flow meter; 24—bottle; 26—separating funnel; 27—distributor; 28—reflux condenser; 29—laboratory autotransformer; 30—quench tube

The chemical conversion takes place in an integrated tubular reactor *7*. The precontact zone (vaporizer) *8* of the reactor is packed with an inert filler (porcelain, quartz, and other materials having grains 1 to 3 mm in size). The catalytic process is conducted in a contact zone *11* containing the catalyst. For the experiment one may use commercial catalysts or catalysts prepared in the laboratory following a prescribed formulation and procedure. The catalyst and filler grains are graded by means of a set of sieves. The quantity of the catalyst is determined by the experimental conditions. In the mid portion of the contact zone of the reactor is arranged a holder for a thermocouple *12*. In the lower part of the reactor provision is made for a side channel to discharge the reaction products.

The thermal section is intended for maintaining the predetermined temperature in the contact zone. The heating is done by a resistance furnace *9* which consists of a steel cylinder with a bore to accommodate the reactor and a duct for a thermocouple, a heating element *10*, thermal insulation *13*, and a casing *15*. The temperature in the reactor and cylinder is monitored by means of a chromel-alumel thermocouple and maintained at the prescribed level with the aid of an automatic control system. Periodic measurements are taken by a portable potentiometer. The temperature is controlled by a voltage regulator (laboratory autotransformer).

The main purpose of the metering section is to feed the stock at a specified rate into the contact zone of the reactor. Alkyl benzenes from the vessels *5* and the diluent from the bottle *6* and intermediate vessels *4* are metered by means of two micropumps *2*. The flow rates of the liquids are checked, if necessary, with the aid of graduated burettes *3*.

In the condensation and separation section, the dehydrogenation products pass through a quench tube *30*; they are condensed and then delivered into a distributor *27* communicating with the atmosphere via a reflux condenser *28*. When other gaseous diluents are used, the reaction products are passed, for complete condensation, through a coil immersed into a liquid or composite coolant. The latter can be any composition having a temperature not higher than —20 °C. The gases are fed into the reactor from bottles *24* through a cleaning system *22*, rheometers *21*, a mixer *20*, and a preheater *19*.

Under stationary conditions, the condensate is sent into a separating funnel *26* to be separated into two portions (the bottom layer being water and the top, hydrocarbons). Under nonstationary conditions (during intervals between sampling), the condensate is accumulated in a collector *25*.

To start the system: (1) Set the pointer of the laboratory autotransformer to zero. (2) Cut in the main knife switch. (3) Energize the heating coils of the furnace by means of the switch on the control panel. (4) Switch on and adjust the temperature measuring instru-

ments. (5) Slowly turn the knob of the laboratory autotransformer to set its pointer to 80-100 V. (6) Open the valve of the water cooling system. (7) Make sure that the vessels *5* and *6*, *3* and *4* contain the starting materials. (8) Fill the vessels *3* and *4* with the starting liquids in the following sequence: (a) close valves B_3 and B_5; (b) open the valves B_1, B_4, B_2, and B_6; (c) fill the vessels *4* and burettes *3* up to the zero mark, and (d) close the valves B_2 and B_6. (9) Reset the three-way valve to discharge the liquid into collector *25*. (10) Feed water into the reactor at 350 °C by (a) opening valve B_3 and (b) switching on the water dispenses. (11) Set the pointer of the autotransformer to 160 V. (12) Heat the furnace to the specified temperature. (13) Switch on the preheater of the gas phase. (14) Feed the gases into the reactor by (a) closing valves B_1, B_{12}, B_8 and (b) opening the reducing valves on bottles *24*. (15) Feed hydrocarbons into the reactor by (a) opening valve B_5 and (b) switching on the hydrocarbon dispenser.

Notes. 1. Items 13 and 14 are included for the case where dilution with the gas phase is involved.
2. If gases are not used, the valve B_8 must be closed.

The temperature is controlled manually by slowly turning the autotransformer knob from 0 to 160 V. In carrying out the experiment it should be borne in mind that the heating element is rated at a power slightly greater than required to attain the necessary temperature. Therefore, when the portable potentiometer ПП-63 produces a signal corresponding to a temperature 10 to 15 °C below the predetermined level, the pointer of the autotransformer must be set to zero, a stable indication must be obtained on the instrument scale, then the pointer must be returned to the mid point of the scale (80-90 V). The temperature may further be controlled by varying the voltage within ± 5 V of the mid value (80-90 V). The temperature fluctuations during sampling must not exceed ± 3 °C of the specified value.

The ЭПП-09 potentiometer is intended for establishing the operating temperature in the furnace and visual observation of temperature changes. Fine temperature control is achieved by means of the portable ПП-63 potentiometer. The emf can be measured by this instrument in the following sequence: (1) Set the switch ON/OFF to position ON. (2) Standardize the potentiometer by (a) setting the switch B_5 to position *C* (control) and (b) zeroing the pointer of the galvanometer with the aid of the knob COARSE and FINE of the rheostat OPER. CURRENT, which is turned with the key COARSE being depressed first, then the key FINE. (3) Take measurements by (a) setting the switch B_5 to position M and (b) positioning the pointer of the galvanometer at zero with the aid of the knobs of the sectionalized switch and slide-wire, turned with the key COARSE being depressed first, then the key FINE. The value of the measured volt-

age in millivolts will be the sum of the readings of the sectionalized switch and slide-wire, multiplied by a factor indicated on the range switch of the potentiometer (0.5, 1, 2). (4) Periodically record the measurement results.

The flow rate of liquid alkyl benzenes and diluents at the reactor inlet is calculated using the following formulas:

mass flow rate of the starting hydrocarbons G (g/h)

$$\sum_{i=1}^{s} G_{1 \cdot i} = G_{1 \cdot 1} + G_{1 \cdot 2} + G_{1 \cdot 3} + \ldots + G_{1 \cdot s} = SV_{h} = \rho V_{h}, \qquad (2.38)$$

where $G_{1 \cdot i}$ is the mass flow rate of the ith component in the stream 1; V_{h} is the volume flow rate of the hydrocarbon stock, in cm^{3}/g; S is the number of components; i is the component number; and ρ is the density of alkyl benzene;

volume flow rate of the diluents (cm^{3}/g)

$$V_{d} = i \sum_{i=1}^{s} G_{1 \cdot i}. \qquad (2.39)$$

To regulate the flow rates of liquid hydrocarbons (V_{h}) and diluent (V_{d}), recalculation must be made to smaller volumes (0.5 to 1.0 cm^{3}).

Liquids are metered at the reactor inlet by means of batch-type piston microdispensers. Their flow rate is checked with the aid of the burettes *4* graduated in 0.1 ml and a stopwatch, with the valves B_{1} and B_{4} closed. The gas flow rate is adjusted by fine adjustment valves B_{13} and B_{14} and monitored by rheometers *21* and a flow meter *23*.

To perform the experiment: (1) Stabilize the temperature and component flow rates. (2) Switch over the three-way valve of the distributor *27* to sampling with delivery of the samples into the vessel *26*. (3) Take 5 to 6 cm^{3} of the condensate. (4) Switch over the three-way valve to discharge into the collector *25*. (5) Remove the separating funnel *26* from the distributor *27*. (6) Separate water from hydrocarbons and transfer it into a flask labeled "Discharge of organic solutions". (7) Put several crystals of $CaCl_{2}$ into a test tube. (8) Decant the hydrocarbons into the test tube and plug it. (9) Paste a label with appropriate marking on the test tube. (10) Carefully wash the separating funnel *26* with acetone then with water and dry it with a jet of air. Decant the washes into a flask labeled "Spent acetone". (11) Connect separating funnel *26* with the condensate distributor *27*. (12) Store the product in a cooler before sending it for chromatographic analysis.

After the experiment: (1) Zeroize the pointer of the laboratory autotransformer by slowly turning its knob. (2) Deenergize the furnace. (3) Disconnect the hydrocarbon metering device. (4) Discon-

nect the water dispenser at 350 °C. (5) Cool the furnace down to 80-100 °C and switch off the temperature measuring instruments. (6) Switch off the water cooling system. (7) Cut out the main knife switch. (8) Disconnect the gas bottles.

Analytical Procedure

The starting alkyl benzenes (stock) and catalytic reaction products are analyzed on a laboratory gas chromatograph ЛХМ-8МД, model 3. The instrument is designed for quantitative and qualitative analysis of gaseous and liquid multicomponent mixtures of organic and inorganic origin, boiling at temperatures of up to 300° C. For design features and performance characteristics of the chromatograph as well as techniques of chromatographic analysis of an alkyl benzene mixture see Work 37. The chromatograms are used to calculate concentrations of components in the analyzed mixtures (stock and alkyl benzene dehydrogenation products).

A typical chromatogram of liquid products of dehydrogenation of alkyl benzene (furnace oil) is shown in Fig. 49. The area of peaks on the chromatogram serves as a basis for quantitative estimation of the component concentrations. The sum of peak areas is assumed to be 100%, and the content of an individual component is calculated from the ratio of component peak areas to the total peak area. This method (Fig. 50) can be used to calculate weight percentages in analyzing components of the same homologous series, and with similar boiling points. The peak area is in most cases determined as that of a triangle. The peak height h from the base (zero) line to the vertex is measured, divided in half, and the distance b between the outer side of one line traced by the recorder pen and the inner side of the other is measured at half the peak height. The peak area is then calculated by multiplying b by h with due account for rescaling.

Exact quantitative data calculated from the areas of individual peaks are obtained by introducing correction factors for each sub-

Fig. 49. Typical chromatogram of liquid products of dehydrogenation of alkyl benzenes:

1—light components (paraffins); *2*—benzene; *3*—toluene; *4*—ethyl benzene; *5*—isopropyl benzene; *6*—n-propyl benzene; *7*—styrene; *8*—α-methyl styrene; *9*—β-methyl styrene

stance. In the separation of a mixture of alkyl and alkene benzenes, the correction factor is assumed to be unity, since for each component a value close to unity has been found experimentally. In the triangle method, measurement is made of the triangle of a respective peak formed by intersection of inflectional tangents to the peak with the zero line (Fig. 50a). In this case, the area of the triangle is calculated either as the product of the height h by the peak width b_p equal to the distance between the points of inflection or as the product of half the height $h/2$ by the width b of the triangle at its base.
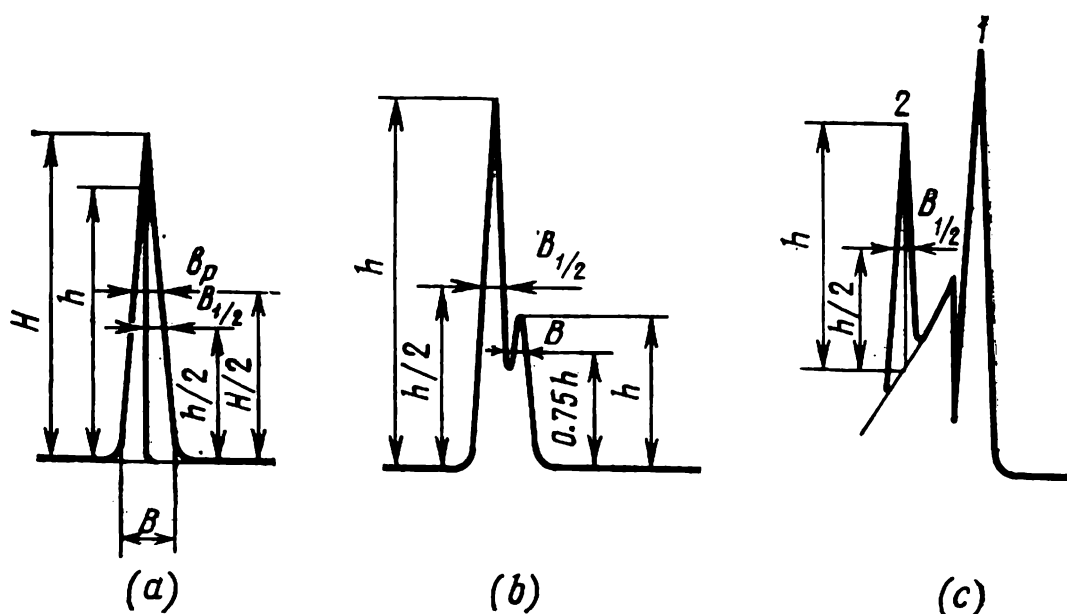
Fig. 50. Different types of chromatographic peaks

a—area calculation by the triangle method; b—incompletely separated peaks; c—low-concentration peak 2 appearing on the rear slope of high-concentration peak 1

The triangle area (in most cases the triangle is not constructed at all) is also determined as the product of the height h by the peak width $b_{1/2}$ at half the height.

In some cases, the method of measuring the peak width at different heights is used. The peak area can be determined using the formula $S = k_2 hb$. The proportionality factor k_2 depends on the intermediate peak height. The values of this factor for calculation of the peak area as a function of the height, at which it is measured, are given below.

Measurement height	0.0	0.60h	0.75h	0.90h
k_2	0.5	1.241	1.654	2.73

With the aid of the factor k_2 one can calculate the areas of incompletely separated peaks (Fig. 50b). Such a picture may be observed in the separation of ethyl benzene and isopropyl benzene. In this case, the accuracy of the method is almost the same as in complete separation.

The peak of *n*-propyl benzene usually appears on the rear slope of that of isopropyl benzene and at higher sensitivity. Here, the peak area is determined in the usual way involving the constructions illustrated in Fig. 50c. In general, the accuracy of peak area measurement depends on that with which the height and width of the peak can be measured. The accuracy is high if the absolute values of the height and width are not too small.

The relative error in measuring the peak area is greater in the case of narrow and short peaks. The optimal ratio between the peak height and its width measured at half the height ranges from 4 to 10. More accurate results are obtained in the case of a symmetrical peak whose asymmetry coefficient $k_{as} = a_2/a_1$ approaches unity (Fig. 50a). The greater the asymmetry coefficient $k_{as} > 1$, the more pronounced the error. The accuracy of peak area measurement by the triangle method varies from 0.3 to 3%.

Drawing Up of the Material Balance and Determination of the Dehydrogenation Process Parameters

The results of chromatographic analysis of the stock and reaction products (liquid catalysate) are used to draw up the material balance and to calculate such basic process characteristics as the percentage conversion, selectivity, and others.

The results of chromatographic analysis of the stock and liquid catalysate for different temperatures are summarized in the following table:

Temperature, °C	Stream number	Concentration of the ith component in the ith stream, Φ_{ii}, wt. %										
		light hydrocarbons	benzene	toluene	ethyl benzene	isopropyl benzene	n-propyl benzene	ethyl toluene	styrene	α-methyl styrene	β-methyl styrene	total yield
t ⋮ t_i												

The material balance is drawn up in the following sequence:
1. Mass flow rate of the hydrocarbon stock

$$\sum_{i=1}^{s} G_{1 \cdot i} = \rho V_h. \tag{2.40}$$

2. Mass flow rate of the ith component of the stock (g/h)

$$G_{1 \cdot i} = \frac{x_{1 \cdot i}}{100} \sum_{i=1}^{s} G_{1 \cdot i}, \qquad (2.41)$$

where $x_{1 \cdot i}$ is the concentration of the ith component in stream 1, in % by weight.

3. The yield of coke and light gases (x_{c+g}) with respect to the hydrocarbons used is determined by weighing, from the difference in the weights of the stock consumed and hydrocarbons in stream 3.

4. Mass coke and gas formation rate G_{c+g} (g/h)

$$G_{c+g} = \frac{x_{c+g}}{100} \sum_{i=1}^{s} G_{1 \cdot i}. \qquad (2.42)$$

5. Mass flow rate of stream 3 (g/h)

$$\sum_{i=1}^{s} G_{3 \cdot i} = \sum_{i=1}^{s} G_{1 \cdot i} - G_{c+g}. \qquad (2.43)$$

6. Mass flow rate of the ith component in stream 3 ($G_{3.i}$) (g/h)

$$G_{3 \cdot i} = \frac{x_{3 \cdot i}}{100} \sum_{i=1}^{s} G_{3 \cdot i}. \qquad (2.44)$$

7. Percentage conversion of the stock component f in stream 1 (%)

$$x_f = \frac{G_{1 \cdot f} - G_{3 \cdot f}}{G_{1 \cdot f}} \, 100. \qquad (2.45)$$

8. Yield of the ith end component of reaction products with respect to the converted stock component f in the stream 1 (i.e. selectivity J of the process)

$$J_{f/i} = \frac{G_{3 \cdot i} - G_{1 \cdot i}}{G_{1 \cdot f} - G_{3 \cdot f}} \, 100. \qquad (2.46)$$

9. Process rate w with respect to the ith component (g/cm³·h)

$$w_i = \frac{G_{3 \cdot i} - G_{1 \cdot i}}{v_{cat}}. \qquad (2.47)$$

The resulting material balance for a particular process temperature (or other specified conditions) is summarized in the following table:

Component	In		Out	
	g/h	wt. %	g/h	wt. %
Light hydrocarbons				
Benzene				
Toluene				
Ethyl benzene				
Isopropyl benzene				
n-Propyl benzene				
Butyl benzenes				
Styrene				
α-Methyl styrene				
β-Methyl styrene				
Coke + gas	0	0		
Total		100.0		100.0

The temperature dependences of conversion, selectivity, and yield of monomers with respect to the consumed stock must be represented graphically.

LITERATURE

Lebedev, N. N., *The Chemistry and Technology of Basic Organic and Petrochemical Synthesis*, 2nd revised and expanded edition, Moscow, 1975, p. 733.

Anderson, R. M., (Ed.), *Experimental Methods of Studying Catalysis*, Moscow, 1972, p. 480.

Instructions to the Laboratory Work
"Catalytic Dehydrogenation of Alkyl Benzenes"

1. Before the experiment, make sure that the setup has been properly assembled and test it for air-tightness.

2. Do not overheat the reactor above 625°C; maintain the temperature in accordance with the assignment.

3. Alkyl benzenes are highly inflammable. Handle them with care: if alkyl benzenes catch fire outside the furnace, put out the flame by sand or a fire extinguisher.

4. Strictly follow the above starting, temperature control and termination procedure.

LABORATORY WORK 17. DEHYDRATION
AND DEHYDROGENATION
OF ETHANOL IN THE PRODUCTION OF BUTADIENE

Ethanol is widely used in the chemical industry, particularly in the manufacture of butadiene-1, 3 (divinyl) which serves as the basic starting monomer in the process of synthetic rubber produc tion, proposed by S. V. Lebedev.

Butadiene is the first member of the homologous series of hydro-carbons with a conjugated system of double bonds: $CH_2=CH-CH==CH_2$. Under normal conditions, butadiene is a gas with a dew point of $-4.3°C$ at which it condenses to form a colourless easily flowing liquid. It can be produced from various starting substances: ethanol, *n*-butane, *n*-butylene, acetylene, and others.

The process, developed by S. V. Lebedev in 1927-28, in which butadiene is synthesized from ethanol and a bifunctional dehydrogenation-dehydration catalyst is used, can be written as the following overall equation:

$$2C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2 - Q$$
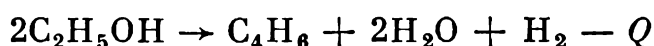
The process is conducted at 375 to 440°C. The main reaction is accompanied by several side ones with the result that other products are formed along with divinyl. The gas mixture at the reactor outlet contains more than 30 substances in commensurate amounts. The theoretical yield of butadiene-1,3 derived from 100% alcohol is 58.7% (the balance being 39.1 of water and 2.2% of hydrogen). The by-products of contact decomposition of ethanol include hydrogen, carbon monoxide, methane, ethane, ethylene, pseudobutylene, higher olefines, toluene, xylene, diethyl ether, and so forth as well as alcohols, aldehydes, ketones, and carbon black forming heavy deposits on the catalyst. The separation of water and hydrogen in the presence of the dehydrating and dehydrogenating components of the catalyst yields, respectively, ethylene and acetic aldehyde. It is precisely acetic aldehyde that serves as the main intermediate product from which butadiene-1,3 is then derived. The action of the catalyst in this process resides in selective decomposition of ethanol with formation of the end products—butadiene, water, and hydrogen. In the absence of a catalyst, the reactions of alcohol dehydrogenation, yielding acetic aldehyde

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2 \qquad (a)$$
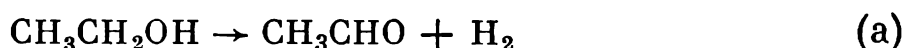
proceed at 450 to 500 °C simultaneously (and almost at the same rate) with the dehydration reactions yielding ethylene:

$$CH_3CH_2OH \rightarrow CH_2 = CH_2 + H_2O. \qquad (b)$$
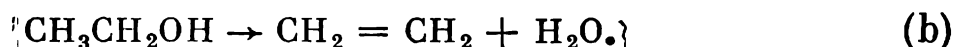
Subsequent reactions between the resulting substances yield various compounds, uncluding but a small amount of butadiene.

A dehydrogenation catalyst (e.g. ZnO) considerably accelerates reaction (a), while reaction (b) is inhibited. As a result, the yield of acetic aldehyde increases substantially, and the process may be conducted at a lower temperature. Similarly, in the presence of a dehydration catalyst (e.g. Al_2O_3), alcohol may be decomposed com-

pletely at a temperature of not less than 400°C with an approximately quantitative conversion to ethylene.

For alcohol decomposition to yield butadiene-1,3, hydrogen, and water as the main products, the catalyst must exhibit a dehydrating, dehydrogenating and condensing capacity at a time. The deposition of carbon on the catalyst mitigates its activity, therefore, the process conducted on the laboratory setup must be periodically discontinued for regeneration of the catalyst. The qualitative composition of the decomposition products is almost independent of temperature (within the specified range) and catalyst activity. At the same time, changes in the catalyst activity affect the quantitative composition of these products. A process with a high yield of butadiene and a minimal amount of by-products can be achieved if a highly active catalyst is used, the stock is free of noxious impurities, the optimal temperature is maintained, and so on.

The efficiency of catalytic decomposition of alcohol is determined by two factors: (1) overall decomposition of ethanol and (2) butadiene yield with respect to the amount of absolute alcohol supplied and decomposed (wt. %). The decomposition of ethanol and butadiene yield depend on the catalyst activity, the rate at which the stock is fed onto the catalyst, and some other factors. The desired activity of the catalyst used for decomposition of ethanol is attained by optimizing the ratio between its dehydrating and dehydrogenating components, as well as by preparing it in such a manner as to ensure uniform blending of its individual components and a developed active surface of the catalyst.

Raising temperature increases the rate of the main reaction, yielding butadiene and speeds up all the side and secondary reactions yielding alcohol decomposition by-products. For example, when the process temperature is raised from 360 to 465°C, the amount of the uncondensable gaseous products increases dramatically. In this case, the butadiene yield is enhanced only in the temperature range of 360 to 440°C. As the temperature is increased from 440 to 465°C, the yield is reduced due to decomposition of butadiene and its being spent in secondary reactions. The ethanol feed rate also produces a tangible effect on the contacting process. The amount of butadiene is maximum at a particular time of contact between the alcohol and catalyst. If the contact time is short, the alcohol decomposition reaction fails to reach completion, and a lot of alcohol "slips" through. In contrast, if the contact between the alcohol and catalyst is too long, the resulting butadiene enters into secondary reactions yielding other products.

This work shows how to determine the yield of butadiene-1,3 resulting from catalytic decomposition of ethanol and introduces the procedure of analyzing the products of this process.

Experimental Setup and Procedure

Figure 51 illustrates the experimental setup for catalytic decomposition of ethanol. The latter is decomposed in a reaction tube *4* placed in an electric furnace *5* and partially filled with a catalyst *6*. The furnace is heated to a specified temperature measured by a thermocouple *3*. The heating of the reaction tube and the catalyst temperature are controlled by a rheostat. Ethanol is fed into the reactor
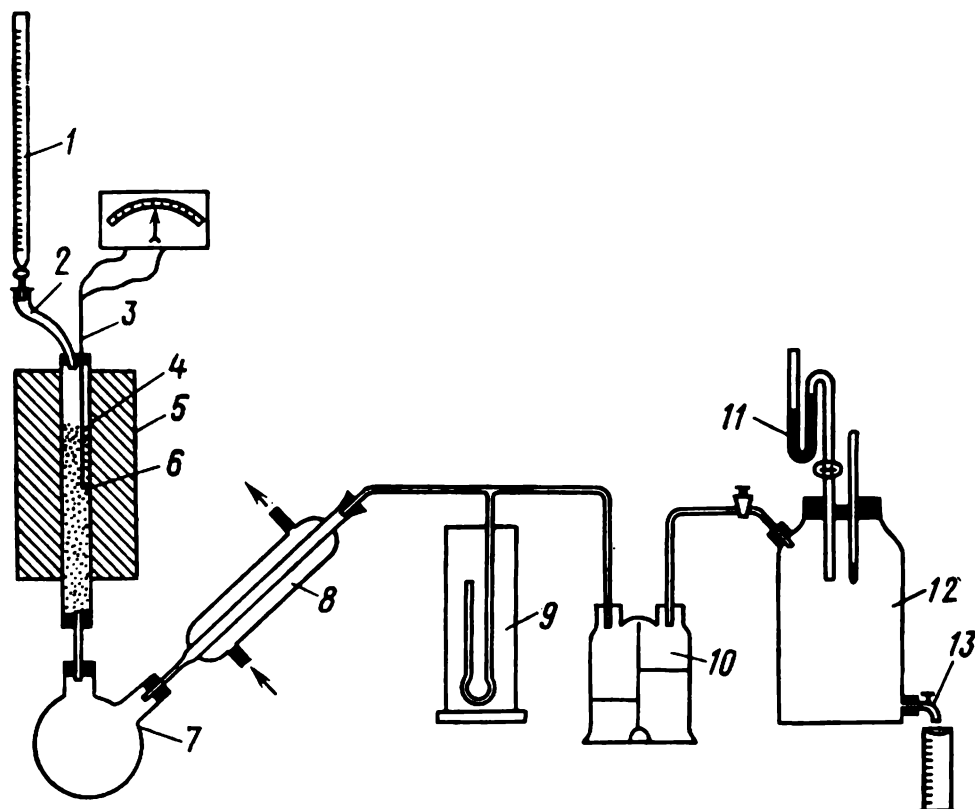
Fig. 51. Experimental setup for catalytic decomposition of ethanol

from a burette *1* via an adapter *2*. The alcohol feed rate is controlled by means of the burette stopcock and monitored by the number of drops emerging from the burette. The front portion of the reaction tube (along the alcohol flow) is packed with crushed quartz, on which the alcohol is evaporated and heated to the contact temperature. The reaction products together with the unreacted alcohol are partially condensed in the receiver *7*, into which they flow from the lower part of the reaction tube, the condensation being more complete in the water-cooled condenser *8*. The pressure downstream of the condenser is measured by a gauge *9*.

The bubble flask *10* filled with a concentrated sodium hydrate solution is intended to trap acetic aldehyde and, partially, diethyl ether. The uncondensable gaseous reaction products flow into a graduated gas holder *12* filled with a saturated solution of sodium salt. To facilitate the discharge of the reaction products and to avoid escape

of gases into the surrounding air during the experiment, a vacuum of 2666 to 3999 Pa must be maintained in the system, which is monitored by a gauge *11* and by the velocity of the liquid seal flowing out of the cock *13*.

Before the experiment, the content of absolute alcohol in the rectified ethanol used must be determined, the catalyst must be loaded into the reactor, and the heating of the furnace to a desired temperature must be controlled. The contents of water and absolute alcohol are worked out by density*. A Tishchenko bottle is weighed on a counter balance to within 0.01 g. Prior to the experiment, the reaction tube is charged with a certain amount (depending on the size of the experimental setup) of an air-dried catalyst in the form of pellets or "worms" produced by mixing the catalyst ingredients in water and rubbing the resulting paste through a metal sieve with 1-mm meshes with subsequent drying to a constant weight and baking.

An aluminium-zinc catalyst may be used or a mixture of activated clay and zinc oxide, prepared as follows: 100 g of powdered pure clay (with a minimal content of iron, calcium, and other impurities) are shaken in a flask with 500 cm^3 of 1 N HCl or H_2SO_4; the mixture is then boiled in a flask with a reflux condenser for an hour. After the solution has been cooled, it is poured out, and the clay is washed by decanting to a neutral reaction. To the washed clay is added a concentrated solution of zinc nitrate or a suspension of zinc hydroxide precipitated in advance in an amount corresponding to the ratio $Al_2O_3 : ZnO = 1 : 1$. The mixture is dried in a thermostat at 150°C, then baked at 600°C in an air flow through a contact tube.

Before proceeding to the experiment, check the experimental setup for air-tightness. To do this, a vacuum is created in the system by means of the gas holder. If the system is completely airtight, air bubbles stop passing through the Tishchenko bottle after several minutes, and the liquid seal no more flows out of the gas holder. Once the system has been found to be airtight, the furnace starts being heated and, at the same time, water is let into the condenser. While the furnace is being heated, the temperature in the catalyst zone is recorded. Then, the burette is filled with alcohol up to the upper graduation marks. The setup is again tested for air-tightness in the heated state, as just-described. If the system is fully airtight, the experiment is begun, and the alcohol feed rate is recorded. Normally, the alcohol, is fed at a rate of a drop per second. The experiment is continued under the preset conditions, and the instrument readings are taken. If the temperature of the catalyst drops when the alcohol starts being fed, it has to be adjusted by varying the resis-

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* The student is given a metal or glass alcoholometer with an instruction for carrying out a particular analysis. In some cases, the alcohol characteristics are specified in the assignment.

tance of the rheostat. The instrument readings are recorded every 10 minutes.

The gaseous products evolving during the experiment are collected in the gas holder. The gas evolution rate is determined roughly from the speed at which gas bubbles move through the Tishchenko bottle; it must be constant. The steady flow of gas is ensured by slowly letting the liquid out of the gas holder and maintaining an appropriate negative pressure in the system by controlling the efflux of the liquid from the gas holder and monitoring the pressure by a gauge. As the gas holder is being filled with gas, the sodium salt solution flows out of it into a special vessel (bottle). The experiment lasts 1.5 to 2 hours, which is sufficient to collect about 5 to 10 dm^3 of the gas depending on the catalyst amount and activity.

As soon as the alcohol supply is cut off, the system is maintained for 5 to 10 minutes in the operating condition for condensation of the residual liquid products and collection of the remaining gas in the gas holder. Then, the receiver 7 with the condensate is heated for 10 to 15 minutes on a water bath to boiling for removal of the gas dissolved in it. The gas holder is then disconnected from the rest of the system, and the furnace is de-energized. After the experiment, the total amount of consumed alcohol is determined along with that of the resulting products. To this end, the contents of the receiver 7 are decanted into a preweighed stoppered flask, and the Tishchenko bottle is disconnected, too. The residual alcohol is weighed on the counter balance, then the flask with the contents of the receiver and the Tishchenko bottle.

The condensate is usually a liquid stratifiable into two layers. The top layer contains a mixture of various hydrocarbons, while the bottom one is essentially a water-alcohol condensate consisting of water, unreacted ethanol, higher alcohols, and a small amount of dissolved hydrocarbons. Both layers are separated with the aid of a separating funnel and transferred into weighed stoppered flasks. Subsequent weighing gives the weights of the hydrocarbon and water-alcohol layers of the condensate. The quantity of the collected gas is measured by the graduations of the gas holder. At the same time, the room temperature is measured, and the atmospheric pressure is determined by means of a barometer. After the amounts of the reaction products have been determined, the gas is analyzed. The results are used to determine the yield of butadiene with respect to the decomposed and supplied alcohol, as well as the yield of by-products.

Analytical Procedure and Calculations

The gaseous products of catalytic decomposition of alcohol are analyzed for content of carbon dioxide, unsaturated and saturated hydrocarbons, oxygen, carbon monoxide, hydrogen, and butadiene.

The gas is analyzed in a conventional apparatus to determine the first six components and in the Korotkov apparatus to determine the butadiene content*. The determination of the latter is based on the interaction between butadiene and maleic anhydride ($C_4H_2O_3$). The method consists in that a premeasured amount of gas is passed repeatedly through liquid $C_4H_2O_3$ at 100°C. The decrement of the
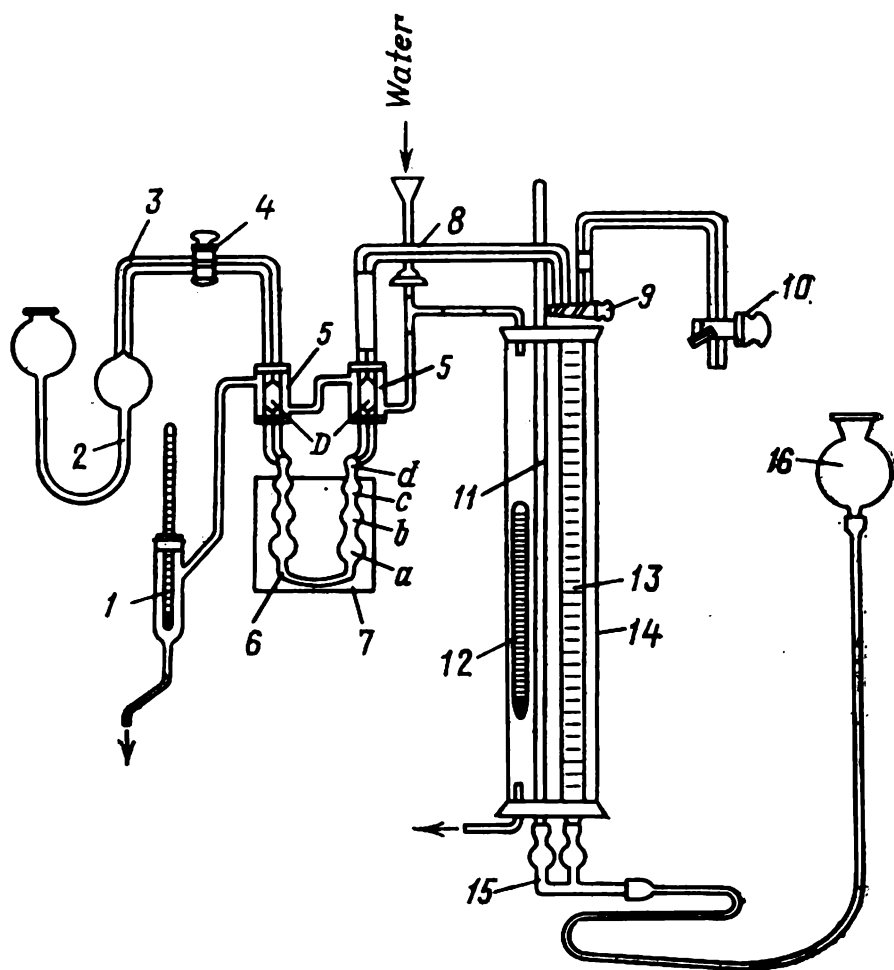
Fig. 52. Korotkov apparatus for gas analysis for divinyl content

1, 12—thermometer; *2*—two-bulb pipette; *3, 8*—capillary; *4*—cock; *5*—cooler; *6*—reactor; *7*—water bath; *9, 10*—three-way cock; *11*—levelling tube; *13*—measuring burette; *14*—glass cylinder with water; *15*—tee; *16*—levelling bottle

gas, expressed in terms of per cent by volume, corresponds to the butadiene content. The gaseous products of dehydration and dehydrogenation of ethanol may also be analyzed chromatographically (see Work 37).

Various instruments are used for analyzing the gas by the above method. Gases containing any amount of butadiene are analyzed

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* To facilitate the analysis, it may be carried out in a single apparatus of the ВТИ type to determine the content of carbon dioxide, all of unsaturated hydrocarbons, oxygen, and carbon monoxide. In this case, the content of hydrogen and saturated hydrocarbons is determined as a difference from 100.

using the Korotkov apparatus (Fig. 52). Its reactor represents a U-shaped capillary tube with five pairs of bulbs. The lowermost pair *a* is intended to accommodate 1.2 to 1.5 g of maleic anhydride. The intermediate pairs *b* through *d* protect against maleic anhydride being carried over from the reactor. The top pair *e*, arranged in coolers *5*, serves to cool and trap maleic anhydride vapours. Water is passed through the coolers, its temperature being measured by a thermometer *1*.

The reactor is placed in a beaker *7* filled with water, which is put on an electric heater and serves as a water bath. The measuring burette *13* having a capacity of 50 to 52 cm³ is graduated in 0.1 cm³ and connected via a three-way cock *9* and a capillary *8* with the reactor *6*. Gas is admitted into the measuring burette *13* through a three-way cock *10*. The burette is enclosed in a glass cylinder *14* filled with water. The latter also houses a levelling tube *11* for exact setting of the mercury level, and a thermometer *12*. The burette and levelling tube communicate via a tee *15* with an overhead levelling bottle *16* filled with mercury. The receiver of the gas emerging from the reactor *6* is a two-bulb tail pipette *2*. Its first bulb is connected to the reactor through a capillary *3* with a cock *4*. All components of the apparatus are secured in a special box or on racks and insulated by asbestos screens from the hot parts—the reactor provided with a water bath and the electric heater.

To start the analysis, the measuring burette is filled to capacity with mercury and the cock *9* is closed. Then, the gas holder with the gas to be analyzed is connected to the three-way cock *10* by a rubber hose, the latter and the burette are several times scavenged with the gas, and the burette is filled with about 50 cm³ of the gas. The mercury levels in the burette and levelling tube are equalized, and the water temperatures at the inlet and outlet are registered. After that, the cocks of the pipette and burette are opened, and the gas is several times passed through the reactor with the overhead levelling bottle with mercury being raised and lowered to maintain the gas volume constant.

The butadiene content may also be determined approximately in a simpler way. For this purpose, a gas analyzer with four absorption flasks is used. The first flask along the gas flow is filled with a potassium hydroxide solution. It is intended to trap the diethyl ether, acetic aldehyde, and small amounts of carbon dioxide present in the gas.

The second flask is filled with 84% sulphuric acid which absorbs butadiene, butylene, and propylene. The practical volume ratio between butadiene and butylenes is 9 to 1. The third flask containing bromine water absorbs ethylene. After ethylene has been absorbed, the gas should be passed, before its volume is measured, through the first pipette for removal of bromine vapours. The fourth flask is filled

with an alkaline solution of pyrogallic acid to trap the oxygen present in the gas as a result of air being sucked into the system. The gas composition data are entered in the following table:

Components	Content, vol. %	Content in terms of air-free gas, vol. %
Aldehydes, diethyl ether, CO_2 Butadiene Butylenes Ethylene Air (in terms of oxygen) Saturated hydrocarbons, hydrogen, CO (determined as the difference)		

The experimental data are used for calculation of the butadiene yield with respect to the supplied and decomposed absolute ethanol. The average experimental temperature is calculated as the arithmetic mean of all readings. The table must also include the values of the minimal and maximal temperatures observed during the experiment.

The stock feed rate is also calculated as the mean of all rates registered over individual time intervals and expressed either in terms of kg/h per m^2 of the cross-sectional area of the reaction tube, or in terms of kg/h per dm^3 of the catalyst, or in terms of kg/h per kg of the catalysts (depending on the available data).

To determine the conversion ratio and the amount of decomposed alcohol as well as to calculate the gas evolution rates, one must know the amount of the undecomposed alcohol, which is found in the decomposition products.

The calculation is based on the amount of the water-alcohol condensate resulting from separation of the liquid decomposition products. It is assumed for simplicity that the water-alcohol condensate contains undecomposed alcohol and water. The amount of water in it is determined as the sum of the amounts of the water introduced with the rectified alcohol and that resulting from the alcohol decomposition reactions yielding ethylene and butadiene. If the unsaturated hydrocarbons (minus butadiene) present in the gas are identified with ethylene, the amount of the water released is calculated in accordance with the equation of the alcohol decomposition reaction

$$C_2H_5OH \rightarrow C_2H_4 + H_2$$
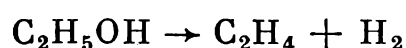
using the formula

$$G'_{H_2O} = \frac{C_{C_2H_4} V 273 P 18}{100 \cdot 22.4 \,(273 + t)\, 1.01 \cdot 10^5}, \qquad (2.48)$$

where $C_{C_2H_4}$ is the assumed concentration of ethylene in the gas, in %; V is the gas volume obtained in the experiment, in dm³; P is pressure, in Pa; and t is the gas temperature, in °C.

The amount of the water (in g) resulting from conversion of the alcohol to butadiene is calculated from the formula

$$G''_{H_2O} = \frac{C_{C_4H_6} V 273 P 36}{100 \cdot 22.4 \, (273 + t) \, 1.01 \cdot 10^5},$$ (2.49)

where $C_{C_4H_6}$ is the butadiene concentration in the gas, in % by volume; V is the gas volume obtained in the experiment, in dm³; P is pressure, in Pa; and t is the gas temperature, °C.

The amount of the unreacted alcohol is determined as follows:

$$G_{alc} = G_{w-a} - G_{H_2O} - G'_{H_2O} - G''_{H_2O},$$ (2.50)

where G_{alc} is the amount of alcohol in the water-alcohol condensate, in g; C_{w-a} is the amount of the water-alcohol condensate, in g; G'_{H_2O}, G''_{H_2O}, and G_{H_2O} are the amounts of water in the rectified alcohol, produced by the formation of ethylene and butadiene from the alcohol, respectively, in g.

The subsequent data processing boils down to calculation of the butadiene yield with respect to the supplied and decomposed ethanol. The butadiene yield (in g) is determined from the butadiene content in the gas and the total amount of the gas and is expressed in terms of weight per cent of the amount of the supplied and decomposed absolute ethanol. The calculation results are tabulated as follows:

Mean experimental parameters		Balance of absolute alcohol			Amount of butadiene produced under normal conditions, dm³	Butadiene content in the gas, g/dm³	Butadiene yield with respect to absolute alcohol, % by weight	
temperature, °C	stock feed rate, cm³/min	supplied, g	returned, g	decomposed, g			supplied	decomposed

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Lebedev, N. N., *The Chemistry and Technology of Basic Organic and Petrochemical Synthesis*, Moscow, 1975.

Proximate Analysis and Inspection in the Manufacture of Synthetic Rubbers/Edited by Isakova, I. A., *et al.*, Moscow, 1970.

Instructions to the Laboratory Work "Dehydration
and Dehydrogenation of Ethanol in the Production
of Butadiene"

1. Assemble the experimental setup, as shown in the diagram, under an exhaust hood far from potential fire sources.

2. Load the catalyst into the reaction tube.

3. Carefully test the apparatus for air-tightness and switch on the heating.

4. **Wear goggles when conducting the experiment.**

5. Maintain the prescribed temperature with the aid of a rheostat.

6. As soon as the prescribed temperature is reached, start feeding alcohol from the burette, maintaining vacuum in the system (several mm Hg).

7. Make sure that the system remains airtight throughout the experiment without any leakage of alcohol and the reaction products.

8. Discharge the catalyst (if necessary) only from a completely cooled reactor.

LABORATORY WORK 18. COPOLYCONDENSATION OF PHENOL AND FORMALDEHYDE

The name "plastics" applied to a vast group of synthetic materials whose basic components are high-molecular compounds (resins) capable of passing to the plastic state at elevated temperatures and pressures, being formed under the effect of external forces, and stably retaining the acquired shape in operation and use. Apart from the high-molecular binding agent, or resin, plastics may contain other components as well, such as fillers (powders, fibrous and membrane materials), plasticizers, colourants, curing agents, stabilizers, and so forth.

The resin is the principal component binding all plastic ingredients into an integral whole and imparting plasticity, mouldability, as well as electrically insulating, corrosion-resistant, and other important properties to the composition. These are also attained by incorporating into plastics cellulose esters, proteins, asphalts, and pitches in addition to the resin.

Cured products based on polycondensation resins can be used over long periods of time in a broader temperature range, and their physicomechanical properties are more stable at higher temperatures as compared to products made of most polymerization resins. On the other hand, resins of this category are more brittle than the polymerization ones.
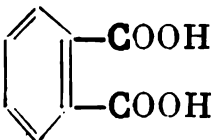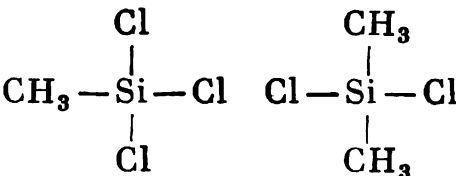
Synthetic resins, just as other high-molecular compounds, are produced by various techniques based on the reactions of polymerization, polycondensation, copolymerization, graft polymerization, and block polymerization.

Since the polycondensation process is exothermic (see Work 4), the molecular weight of the end products at equilibrium will be greater at a lower temperature. This is why, to attain a high process rate, it is common practice to initially conduct polycondensation

at an elevated temperature, then reducing it in approaching the state of equilibrium to derive a product with a greater molecular weight.

Catalysts augment the polycondensation rate, whereby the entire system approaches equilibrium within a shorter space of time. The equilibrium constant of processes yielding polyesters is $K \cong 4$, while that of phenol-formaldehyde resin formation processes is $K = 10\,000$. Hence, in the latter case the equilibrium is shifted toward the end products, and the water formed as a by-product exerts practically no effect on the kinetics of the polycondensation process. If the starting components contain two functional groups each, polycondensation results in a linear polymer. And if a starting component includes a greater number of functional groups, the result is a three-dimensional polymer. The more complete the removal of low-molecular by-products from the reaction zone, the greater the molecular weight of the polymer; otherwise, by-products initiate the process of degradation.

At particular steps of polymer production, the intermediate compounds have a linear or branched structure, and only the final steps involve reactions resulting in a three-dimensional structure. The linear structure of polymers is responsible for their capacity to melt and dissolve in some solvents, whereas three-dimensional polymers are nonmelting, insoluble, and exhibit excellent mechanical properties. The polycondensation process is conducted in a melt, at the interface between two phases in solution. The most widely spread polycondensation resins are:

Resins	Starting Monomers
Phenol-formaldehyde	Phenol C_6H_5OH and formaldehyde CH_2O
Urea-formaldehyde	Urea $CO(NH_2)_2$ and formaldehyde CH_2O
Alkyd (polyester)	Polybasic acids, such as phthalic acid

and polyhydric alcohols, such as glycerol
$CH_2OH-CHOH-CH_2OH$

Polyamide	Polybasic acids, such as adipinic acid $HOOC(CH_2)_4COOH$, and amines, such as hexamethylene diamine
Organosilicon (silicone)	Mono- and dimethylsilicon chlorides

The rate and direction of polycondensation reactions as well as the composition and nature of the resulting compounds depend on

the ratio between the reactants and their properties, number of functional groups, area of contact between the reactants (mixing conditions), temperature, removal of low-molecular by-products (to shift the equilibrium), and type of the catalyst involved. The calalysts of polycondensation include acids, alkalis, and salts [HCl, H_3PO_4, $(COOH)_2$, NaOH, NH_4OH, etc.]. Depending on the catalyst amount and type and the ratio between the starting monomers, the reaction yields either thermoplastic (thermosoftening) or thermoreactive (thermosetting) resins.

The thermoplastic resins, having a linear structure, melt when heated, resolidify when cooled, and dissolve in certain solvents. The thermoreactive resins, characterized by a cross-linked two- or three-dimensional structure, on the contrary, pass into a nonmelting and insoluble state when heated or stored for a long time.

In the laboratory experiment, the polycondensation resin is synthesized from phenol and formaldehyde. When phenol is in excess and a mineral acid is used as the catalyst, the process yields novolac resin, or simply novolac. To render the resin nonmelting, formaldehyde or hexamethylene tetraamine (urotropin) $(CH_2)_6N_4$ is added, which also speeds up curing [when heated, it decomposes into CH_2O and NH_3]. Thus, the production of phenol-formaldehyde resin is a homogeneous catalytic process (the starting substances and catalyst being in the liquid phase) which, however, yields a heterogeneous system L-L-insolubles. The equation of the novolac-yielding reaction can be written as

$$nCH_2O + (n + 1)C_6H_5OH \rightarrow H[C_6H_3(OH)CH_2]_nC_6H_4OH + nH_2O.$$

The equilibrium constant of the reaction reaches a high value ($k = 10\ 000$), that is the reaction proceeds, in fact, toward formation of the resin. The water released during the process produces but an insignificant effect on its equilibrium and rate, the basic factors determining the direction of the reaction and its kinetics being temperature, reaction time, catalyst species and concentration. The lower the molar ratio of phenol to formaldehyde, the greater the molecular weight of the resulting resin. Increasing the polycondensation time leads to a more complete combination of phenol with formaldehyde and to a greater average molecular weight of the end products. When the aldehyde is in excess (seven and more moles of formaldehyde per six moles of phenol) and an alkali or an alkali salt is used as the catalyst, the products are thermoreactive or resol resins. In this case, up to 1.5 moles of formaldehyde are combined with one mole of the reacted phenol. Ultimately, the condensation reactions yield three-dimensional molecules. However, phenol reacts with formaldehyde in a stepwise manner, yielding various compounds at different steps of the process, and a complex mixture of isomers and polymer-homologues capable of entering into subsequent reac-

tions yielding more complex condensation products is formed in the course of the process. This variety is due to the fact that the nucleus of phenol contains three mobile hydrogen atoms capable of entering into substitution reactions.

Depending on the curing stage, three types of resol resins are recognized: (a) resol (bakelite A)—a mixture of high-molecular products, melting when heated, soluble in alcohol or acetone, and having a linear structure; this stage is attained at 70 to 75 °C; (b) when heated to 90°C or stored for a long period of time, resol becomes resitol (bakelite B) having a branched structure. It dissolves in alcohol or acetone but partially, swelling considerably in doing so, does not melt when heated but softens passing into an elastic state, and can be completely dissolved in solvents; (c) resite (bakelite C)— the last step of polycondensation is involved in the manufacture of finished articles (at a higher temperature and pressure); resite does not soften when heated and does not swell in solvents; this curing process consists in linking of long linear chains by transverse bonds:
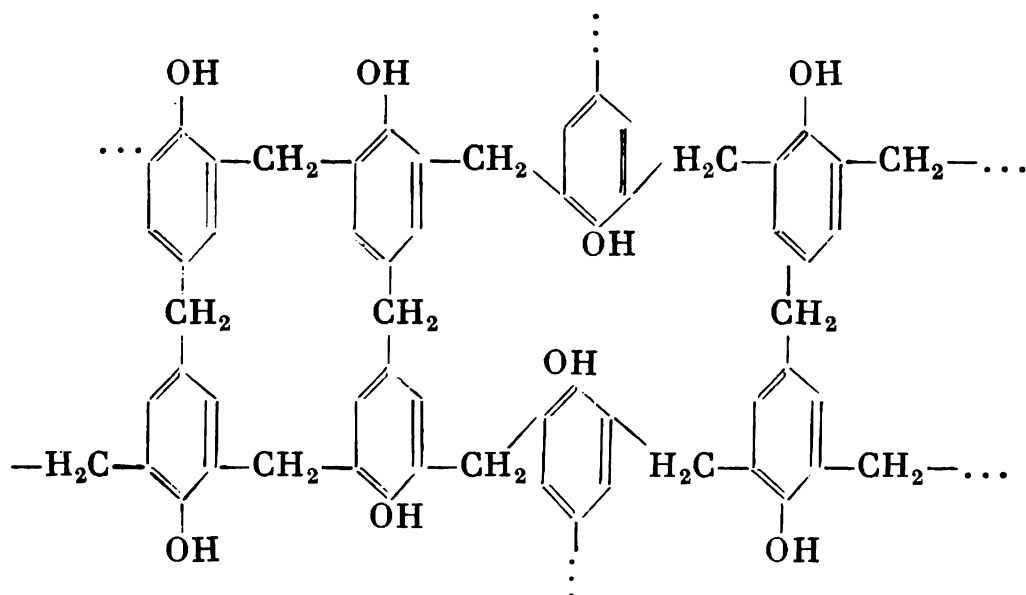
Resol resins are more difficult to produce than novolacs because of their tendency to pass into resitol. This is why for each resin grade its own polycondensation time is strictly specified, which, if exceeded, results in a higher viscosity of the resin.

This work includes: (1) synthesis of a novolac or resol resin (according to the assignment) by copolycondensation of phenol and formaldehyde, followed by determination of its yield, and (2) introduction of the most typical procedures of analyzing polycondensation resins.

Experimental Setup and Procedure

The specified mixture of crystalline phenol and formaldehyde in the form of an aqueous solution (formalin), stirred till complete dissolution of phenol, plus a prescribed amount of the catalyst are

charged into a three-necked round-bottomed flask *1* in a bath *2*
(see Fig. 17). Into the middle (largest) neck of the flask is inserted
a reflux condenser fitted into a plug. One of the side necks of the
flask accommodates a thermometer *6*, while the other is plugged
or receives a dropping funnel *4*. Passing through the inner tube
of the condenser *5* is a stirrer *3* driven (from above) by a
motor.

Phenol and formalin taken to produce novolac in a molar ratio
of 1.12-1.42 to 1 are mixed in the flask at room temperature. After
dissolution of phenol, the catalyst in the form of 1 N HCl or 1 N
H_2SO_4 (1 to 1.5% of the phenol weight) is introduced into the flask,
and the latter is placed in the bath heated to 90-100 °C. The reaction
is conducted until the separated water layer stops changing in
volume and qualitatively reacting to formaldehyde.

To monitor the course of the reaction, one can periodically sample
the reaction mixture through the second side neck of the flask and,
by cooling the samples, determine the end of the reaction by appear-
ance of a stable cloud. It is even more preferable to transfer a 3 to
5 cm^3 sample into a porcelain cup. The cup is heated on the burner
flame for evaporation of excess water, then cooled, and it is deter-
mined by observation whether the resin solidifies or not. If the mixture
is heated rapidly after the catalyst has been introduced (by changing
over to a very hot water bath), frothing and spattering of the reac-
tion mass from the flask may occur.

Attention should be paid to the intensity of the reaction between
phenol and formaldehyde. Under normal conditions, the mixture is
heated to 90-95 °C. If the reaction becomes vigorous (usually 20 to
40 minutes after heating) and the liquid starts to boil intensively, the
heating should be immediately stopped and the flask removed from
the bath. The reaction then goes on without additional heating
(sustained by the heat of the condensation reaction with the tem-
perature rising to 100 °C). As soon as the vigorous reaction is over,
the flask is again placed in a hot water bath, and the heating is con-
tinued until the mixture stratifies into two distinct layers. When
it is established that the reaction between phenol and formaldehyde
is over, the heating is stopped and the water layer is allowed to
stand. Then, the water layer is decanted, and the resin is rapidly
(before it is cooled) transferred into a porcelain cup and dried first
on a water then a sand bath with continuous stirring by a glass rod
at a temperature not higher than 130-160 °C. The drying is discon-
tinued when the resin drop solidified on the rod can be easily crushed.
After drying, the resin is weighed, and its yield with respect to the
starting reagents is determined (for this purpose, the porcelain cup
in which the resin was dried must be weighed in advance). Then, the
resin is poured onto an iron sheet, cooled, crushed in a mortar, and
subjected to different tests.

The reagents are usually calculated with reference to 50-100 g of phenol*. Tentative formulations of the initial mixtures are listed in Table 10.

Table 10

Phenol: formaldehyde, mole: mole	Catalyst, percentage of phenol		Crystalline oxalic acid, g	Phenol: formaldehyde, mole: mole	Catalyst, percentage of phenol		Crystalline oxalic acid, g
	HCl, m. p. 1.19	H_2SO_4, m. p. 1.84			HCl, m. p. 1.19	H_2SO_4, m. p. 1.84	
1.4	1.0	—	—	1.8	—	0.3	—
1.4	—	0.3	—	2.0	1	—	—
1.4	—	—	1	2.5	1	—	—
1.5	1	—	—	3.5	1	—	—
1.5	—	0.3	—	10.0	1	—	—
1.8	1	—	—				

To carry out the synthesis, 100 g of phenol, for example, 100 g of 37% formalin, and 6 g of a 25% aqueous solution of ammonia (1 mole of phenol, 1.16 moles of CH_2O, and 1.5 wt.% of NH_3 of the phenol weight) are charged into a 500-cm³ round-bottomed flask (see Fig. 17). The flask is coupled to a reflux condenser and heated on a water bath with stirring. The mixture is heated slowly to its boiling point (90-95°C). The mixture is boiled for 10 to 15 minutes till the condensation reaction is over. To determine whether the reaction is over, a sample is taken from the flask for measuring the cloud point of the reaction mixture. To this end, the flask is unplugged, and 2 to 3 cm³ of the reaction mixture are taken by a pipette and transferred into a test tube of standard size. A thermometer graduated in 1° is inserted into the test tube with the sample, and the tube is cooled with shaking down to 10 °C. As soon as persistent clouding begins, the process is discontinued. If the sample is not yet cloudy, heating continues at the same temperature for another 10 to 15 minutes, and the cloud test is repeated. This is done every 10 to 15 minutes of heating till the sample becomes cloudy.

After the test, the heating is carried out for another 10 minutes. Then, the heater and stirrer are switched off, the reflux condenser is disconnected, the flask is removed, and its contents are transferred into a porcelain cup. The latter is allowed to cool, after which the upper water layer is decanted. The resin remaining in the cup is then washed several times with water to a neutral reaction, and the cup with the resin is weighed. This is how the weight of the resin obtained in the experiment is determined.

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* If the phenol contains water, an appropriate correction factor must be used in the calculations.

The resulting resol resin is a sticky substance varying in colour from yellow to brown. If overheated above the specified temperature, the resin may pass into a solid, nonmelting and insoluble state (resite).

To assess the end product, the following parameters are determined in addition to its yield: (a) water content; (b) softening and melting points; (c) polymerization rate (i.e. the time it takes for the resin to cure on a heater); (d) molecular weight calculated from the resin yield; (e) molecular weight determined by the Rast method; and (f) content of free phenol in the resin.

1. Determination of the Water Content in Novolac. The water content in the resin is determined by distilling water off in the presence of xylene by the Dean-Stark method (see Fig. 25). An amount of 5 to 10 g of the resin (weighed to within 0.01 g) is dissolved in 30 to 50 g of dehydrated xylene, and the solution is poured into a round-bottomed flask having a capacity of 300 cm³ with another 50 cm³ of xylene being added into the latter. The flask is connected to a Dean-Stark apparatus with an Allihn condenser and heated on a sand bath. The forming azeotropic mixture of water vapours and xylene is condensed in the condenser and collected in a graduated receiver. The xylene accumulating in the top layer flows back into the flask, while the water stays in the lower part of the receiver. The mixture is boiled until the water layer stops growing and the xylene on top of the water becomes clear. The amount of water (v_{H_2O}) in the receiver is measured at the end of the test (two and more hours after settling) after all other tests have been completed and expressed as percentage of the resin weight G_g:

$$\% \text{ water in the resin} = v_{H_2O}100/G_g.$$

2. Determination of the Softening and Melting Points of Novolac. The softening point of the resin is the temperature at which the finely divided powder starts caking (agglutinating), whereas the melting point is the temperature at which the resin ceases to be a powder and starts melting.

There are different methods for determining the softening and melting points of the resin. The most common are: (1) determination of the softening and melting points in a capillary and (2) determination of the resin softening point by passage of a weighed amount of mercury through a resin layer of a particular thickness. Depending on the assignment, the determination is carried out using one of the two methods.

To determine the melting and softening points of novolac in a capillary use is made of an apparatus (Fig. 53) consisting of a test tube at least 150 mm long with a wide bottom, into which glycerine is poured. A second test tube forms a ground-glass joint with its opening, into which a thermometer 6 to 8 mm in diameter and

graduated from 0 to 200°C is inserted through a plug. This apparatus can be replaced by a different arrangement in which a 300-cm³ conical flask is filled with 200 cm³ of glycerine, and a tube with a thermometer is inserted into it through a plug so that its lower end immersed into the liquid is at a distance of 13 mm from the flask bottom. The flask and test tubes are perforated to allow for air circulation.

Approximately 0.01 g amounts of the finely divided resin are placed into thin-glass capillaries 10 to 15 mm in height and 1.5 mm in internal diameter, with a sealed end. The resin is charged into the capillaries in such a manner that after careful ¦compaction it forms a core 3 to 4 mm high. To this end, the resin in a capillary is carefully compacted with the aid of a glass capillary (filament) having a smaller diameter or by letting the capillary with the resin drop freely at least twenty times through a 0.5 m long glass tube. Two capillaries packed in this fashion are attached to a thermometer by means of a thin rubber thread. The capillaries are arranged so that the resin cores are level with the mercury bulb of the thermometer. The thermometer with the capillaries are mounted in the apparatus so that the thermometer bulb is below the liquid level. Then, the assembly is heated by a gas burner through an asbestos net so that at the beginning (the first 10 to 15 minutes) the temperature rises at a rate

Fig. 53. Apparatus for determining the melting and softening points

1—flask with glycerine; *2*—tube; *3*—thermometer; *4*—capillary with resin

of 5 degrees per minute, and after 40°C the heating proceeds at a rate of 1 deg/min. The temperature at which individual particles of the powdered resin start caking is registered as the resin softening point. The heating is continued up to a temperature at which the resin ceases to be a powder. This temperature corresponds to the resin melting point. The determination is repeated several (two or three) times, and the average of the measured values is taken. The difference between the values taken during different measurements must not exceed 1°C.

The softening point determined by passing mercury through a resin layer is the temperature at which a 5 mm high resin layer heated in a glass tube having an internal diameter of 6 mm is pierced by 5 g of mercury placed above the resin layer in the same tube. The apparatus for determining the softening point comprises two beakers, the external beaker being 8 cm in diameter and 15 cm high, while the internal beaker is 6 cm in diameter and 10 cm high. The internal

beaker is closed by a cover in which five holes are made and attached to the external beaker through a metal disc (Fig. 54). The holes in the cover of the internal beaker receive a thermometer and four glass tubes 6 mm in diameter. The ends of the tubes are ground, and the tubes are marked exactly at 5 mm from one end. They are filled with the resin up to the mark, the resin is compacted from above by a glass rod, and the excess resin is cut off from below by a heated knife.

The tubes filled with the resin are secured on the cover of the internal beaker so that the resin is level with the mercury bulb of the thermometer. The external beaker is filled with glycerine up to half the height of the internal beaker. Then, 5 g (i.e. 0.367 cm³) of mercury are transferred into each tube from a microburette. The apparatus assembled in this manner is put on a tripod and slowly heated through an asbestos net at a rate of one or two degrees per minute. The heating continues till the mercury breaks, by gravity, through the layer of the softened resin and flows into the internal beaker. The temperature reading at this moment corresponds to the resin softening point. This determination is ,repeated several times, and the arithmetic mean of all readings is taken as the softening point.
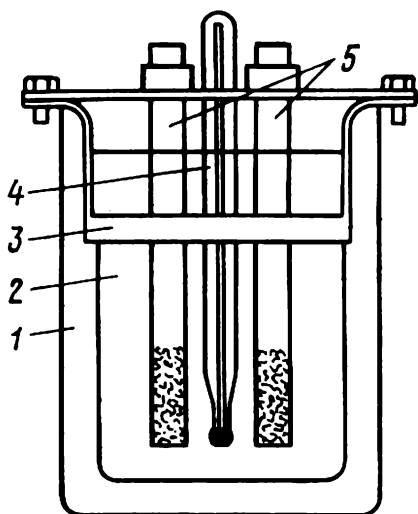
Fig. 54. Apparatus for determining the softening point by the mercury method

1, 2—external and internal beakers; *3*—metal ring; *4*—thermometer; *5*—glass tubes

3. Determination of the Resin Polymerization Rate. By the resin polymerization rate is meant the time it takes for 0.5 g of powdered resin to pass into a nonmelting state on a metal plate heated to 160°C. The weighed amount of powdered resin must be placed on the plate so that the contact area does not exceed 1 cm². As soon as the powder is transferred onto the plate, it starts being stirred by a glass rod with time being registered by a stopwatch. The moment at which the resin stops being pulled by the rod and a solid crust is formed is taken to be the end of polymerization, as marked by the stopwatch. To determine the polymerization rate of novolac the latter is premixed in a mortar with hexamethylene tetramine $(CH_2)_6N_4$ (taken in an amount equal to 14% of the resin weight). To determine the polymerization rate of resol, the latter is taken in its pure form.

The determination is repeated several times, and the mean value of all measurements is taken. The polymerization rate of the resin is a relative characteristic.

4. Determination of the Molecular Weight of Novolac from the Resin Yield with Respect to Formaldehyde. Usually, the molecular weight of the resin is determined by the cryoscopic method with selection of an appropriate solvent (phenol, camphor, etc.) or spectroscopically. In the simplest case, the molecular weight of novolac can be determined from the resin yield with respect to formaldehyde. As has been established experimentally, phenol novolac is essentially a mixture of polyphenols of the structure

$$HOC_6H_4CH_2-[C_6H_3(OH)CH_2]_{n-1}-C_6H_4OH$$
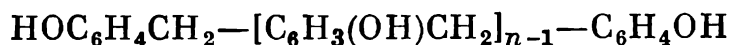
with an average degree of condensation $n = 5$ (usually $n = 4\text{-}8$). Novolac resin can be considered as a mixture of polyphenols of various degrees of polymerization, consisting of $(n + 1)$ aromatic nuclei interlinked through CH_2 groups. The formula of novolac can be rewritten as follows:

$$H[C_6H_3(OH)CH_2]_n-C_6H_4OH$$

Then, the mean molecular weight M of novolac can be expressed as

$$M = 106n + 94.... \qquad (2.51)$$

If the resin yield per mole of formaldehyde is expressed as X, the corresponding formula takes the form $M/x = n$ (i.e. one can determine the number of moles of formaldehyde involved in the formation of a resin molecule), or, in accordance with Eq. (2.51),

$$n = (M - 94)/106 = M/X,$$

hence,

$$M = 94X/ (X - 106). \qquad (2.52)$$

Knowing exactly the weight of the resulting resin, one can calculate the molecular weight of the product from the above formula and, consequently, determine the degree of polymerization. A more accurate way to determine the resin yield is as follows: (1) the reaction flask is weighed when empty, then after the reaction with the resulting novolac, and (2) the water and free phenol contents in the product are determined. Subtraction of the water and free phenol contents from the total weight of the product gives the weight of pure novolac.

5. Determination of the Molecular Weight of Novolac by the Cryoscopic (Rast) Method. The method is based on the ability of the solute to bring down the melting point of the solvent, which depends on the ratio between the number of solute molecules and that of the solvent ones, as well as on the properties of a given solvent characterized by its cryoscopic constant.

The best solvent for the purpose is camphor whose cryoscopic constant is 8 times greater than that of benzene and 12 times greater than that of water. Camphor can be used for substances soluble in

molten camphor, stable up to 190°C and having a molecular weight of 300 to 400.

The molecular weight of novolac is determined using an apparatus shown schematically in Fig. 55. An amount of 10 mg of finely divided novolac is charged into a tube, pushed inside by a thin glass rod, and weighed on an analytical balance to within 0.1 mg. In the same way, 100 to 125 cm³ of camphor are inserted into the tube, and the weighing is repeated. The tube is wrapped in wet filter paper and sealed on a small flame, being pulled into a thick filament. The resulting ampoule is inserted into the apparatus and starts being heated till the camphor fuses with the resin, the solution being agitated by rotation of the ampoule. The contents of the latter are then cooled till crystals start to precipitate, and the ampoule is reinserted into the apparatus after being tied to a thermometer. The temperature is slowly raised, and the melting is observed. The melting point is considered to be the temperature

Fig. 55. Apparatus for determining the molecular weight of novolac

1—round-bottomed flask; *2*—tube with resin; *3*—thermometer

at which the last crystal disappears. The molecular weight of the resin is determined from the formula

$$M = 40G_\mathrm{r}1000/G_\mathrm{c}\Delta t, \qquad (2.53)$$

where 40 is the cryoscopic constant of camphor; G_r is the weighed amount of novolac, in g; G_c is the weighed amount of camphor, in g; Δt is the melting point of camphor minus that of the solution (the melting point of camphor is 176°C).

6. Determination of Free Phenol. An accurately weighed amount (about 2 g) of the resin is dissolved in 15 cm³ of ethanol, and free phenol is distilled off with water vapours (Fig. 56). The distillation is stopped when no more phenol is present in a sample of the distillate with bromine water. After the total volume of the distillate has been measured, two 100-cm³ samples are taken from it and analyzed for phenol content.

This method of phenol determination is based on substitution of hydrogen by bromine in the benzene nucleus in the reaction
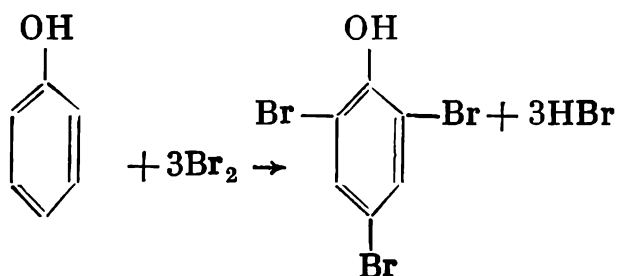
When free bromine is in excess, the reaction is quantitative. If the reaction mixture is allowed to stand for a long period of time, the bromination proceeds further yielding triphenolbromine:

$$\text{Br–}\underset{\overset{|}{\text{Br}}}{\overset{\overset{\text{OH}}{|}}{\bigcirc}}\text{–Br} + Br_2 \rightarrow \text{Br–}\underset{\overset{|}{\text{Br}}}{\overset{\overset{\text{OBr}}{|}}{\bigcirc}}\text{–Br} + HBr$$
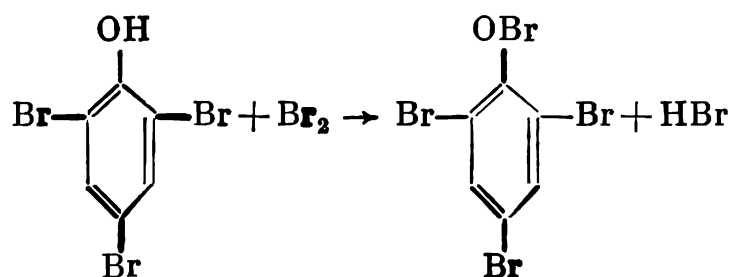
When a potassium iodide solution is added to the reaction mixture, free bromine plus the bromine that has substituted the hydrogen in
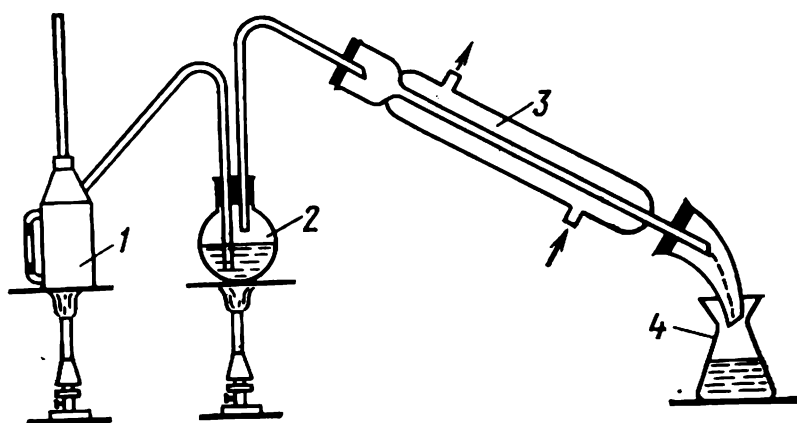
Fig. 56. Apparatus for determining free phenol
1—vaporizer; *2*—flask; *3*—cooler; *4*—receiver

the hydroxy group displace an equivalent amount of iodine from KI, according to the equation
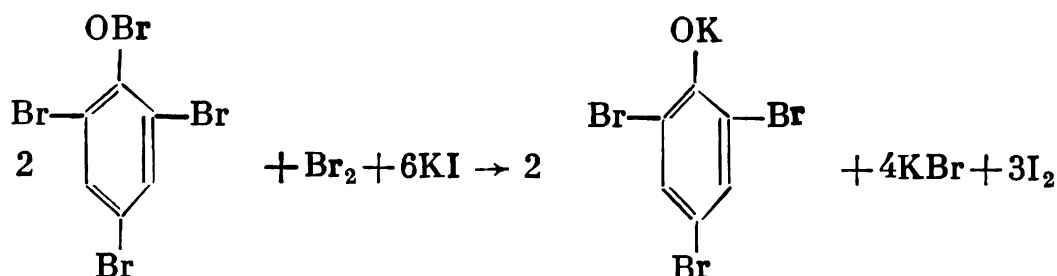
$$2\,\text{Br–}\underset{\overset{|}{\text{Br}}}{\overset{\overset{\text{OBr}}{|}}{\bigcirc}}\text{–Br} + Br_2 + 6KI \rightarrow 2\,\text{Br–}\underset{\overset{|}{\text{Br}}}{\overset{\overset{\text{OK}}{|}}{\bigcirc}}\text{–Br} + 4KBr + 3I_2$$

The separated iodine is titrated with $0.1\ N$ $Na_2S_2O_3$ in the presence of starch:

$$3I_2 + 6Na_2S_2O_3 \rightarrow 6NaI + 3Na_2S_4O_6$$
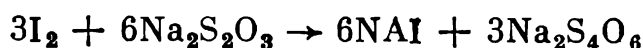
An exact amount of phenol is charged into a 100-cm^3 measuring flask, made up with distilled water up to the mark, and thoroughly stirred. Then, two samples are pipetted from the flask (10 to 20 or 25 cm^3 each) and transferred into a 250-cm^3 stoppered flask. An amount of 50 cm^3 of a bromide-bromate solution (containing 5.939 *g*

of KBr and 1.666 g of KBr_2O_3 per cubic decimetre of water) is added together with 5 cm³ of concentrated H_2SO_4, and the mixture is shaken. Ten minutes later, 10 cm³ of a 10% KI solution is added, and the separated iodine is titrated with a $Na_2S_2O_3$ solution. At the same time, a control test is carried out, in which the same amount of distilled water is added instead of phenol.

The reaction equations suggest that 1 cm³ of 0.1 N $Na_2S_2O_3$ corresponds to 0.00156 g of phenol. In that case, its amount will be

$$G = (a - b) F\ 0.00156, \qquad (2.54)$$

where a is the amount of 0.1 N $Na_2S_2O_3$, spent in the titration during the control test, in cm³; b is the amount of 0.1 N $Na_2S_2O_3$, spent in the titration during the main test, in cm³; and F is the normality factor of 0.1 N $Na_2S_2O_3$.

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Toroptseva, A. M., Belgorodskaya, K. V. and Bondarenko, V. M. *Laboratory Works in the Chemistry and Technology of High-Molecular Compounds*, Leningrad, 1972, pp. 199-206.

Chemical Technology, Mukhlyonov, I. P., Averbuch A. Ya., et al., Moscow, 1979.

Instructions to the Laboratory Work "Copolycondensation of Phenol and Formaldehyde"

1. Make sure that the experimental setup has been properly assembled and that the stirrer works normally.

2. Charge calculated amounts of the reagents into a flask and add the catalyst dropwise.

3. Tightly close the perforations in the reaction flask.

4. Switch on the water cooling of the condenser and heat the water bath.

5. When using a gas burner to heat the water bath, make sure that the flame does not flash back.

6. Weigh the porcelain cup for decanting the resin with water.

7. As soon as the mixture in the flask starts boiling vigorously, stop heating the water bath and remove it.

8. Evaporate water from the resin only on a sand bath under an exhaust hood to avoid intoxication with the mixture vapours. Dry the mixture at normal pressure, gradually raising the temperature and stirring the resin.

LABORATORY WORK 19. CATALYTIC PROCESSES OF FORMALDEHYDE PRODUCTION

Formaldehyde is one of the most voluminous products of organic synthesis. It is used in the manufacture of plastics (polyformaldehyde, urea-formaldehyde, phenol-formaldehyde, etc.), isoprene and polyisoprene rubber on its basis, as well as in the synthesis of

many drugs, tannins, explosives, and dyes; it is also used as a disinfectant, antiseptic, and deodorant.

At present, formaldehyde is produced by catalytic conversion of methanol, heterogeneous or homogeneous oxidation of methane and its closest homologues (propane and butane), and incomplete oxidation of dimethyl ether.

A. CONVERSION OF METHANOL

Methanol still remains the basic source of formaldehyde production which may involve the following processes:

(a) partial oxidation of methanol over metallic catalysts (Ag, Cu) with atmospheric oxygen taken in an insufficient amount as compared to what is required theoretically;

(b) incomplete oxidation of methanol with atmospheric oxygen over oxide catalysts (e.g., a mixture of 17.5% of Fe_2O_3 and 82.5% of MoO_3).

In either case, it should be borne in mind that at 60°C and below the limits of the explosive range equal 6-8 to 25-37% of methanol in air (the higher the temperature, the broader the range), which is why the process must be conducted within the safe limits.

According to the former process, steam is added to an air-alcohol mixture containing more than 37% of methanol, and the whole is passed through a fixed catalyst bed (silver on pumice) at 650 to 700°C. Under these conditions, methanol is dehydrogenated and oxidized according to the following reaction equations:

$$CH_3OH \rightarrow CH_2O + H_2 - 85.3 \text{ kJ} \tag{a}$$

$$CH_3OH + 0.5O_2 \rightarrow CH_2O + H_2O + 156.5 \text{ kJ} \tag{b}$$
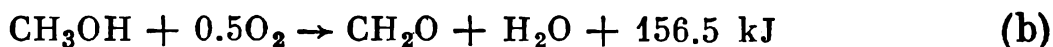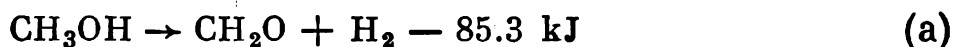
Formaldehyde is partially lost as a result of the reactions

$$CH_2O \rightarrow CO + H_2 - 5.4 \text{ kJ} \tag{c}$$

$$CH_2O + O_2 \rightarrow CO_2 + H_2O + 436 \text{ kJ} \tag{d}$$

In addition, the conversion process is complicated by oxidation of the released hydrogen and some other reactions. The overall thermal effect of the process is positive (exothermic). All of the catalysts used in this process speed up reactions (a) and (b) in a selective manner, therefore, the volume velocity is usually high and in the case of a silver catalyst it is in the neighbourhood of 8000 h^{-1}. As the residence time increases, the yield of formaldehyde may decrease as a result of reactions (c) and (d) as well as other side reactions. In order to avoid decomposition of the forming formaldehyde downstream of the catalyst bed, the reaction products (contact gases) are rapidly cooled (quenched) in a tubular cooler, or with the

aid of a water jacket, or by direct injection of water (or formalin) immediately downstream of the catalyst bed. Apart from formaldehyde, hydrogen, and carbon oxides, contact gases may also contain small amounts of methane (as a result of hydrogenation of methanol and other side reactions), as well as traces of formic acid.

Thus, the yield of the main end product—formaldehyde—is affected by the following process parameters: (a) temperature of the conversion process; (b) ratio of methanol to atmospheric oxygen in the initial mixture; (c) volume velocity (contact time); and (d) properties of the contact.

Raising the process temperature accelerates the above reactions and shifts the equilibrium of reaction (a) toward the end products. However, main reactions (a) and (b) are sped up along with side reactions, particularly (c) and (d). Therefore, in order to minimize their effect on the yield of the main product, the conversion must be conducted within a narrow temperature interval. The conversion of methanol to formaldehyde in accordance with reaction (b) is accompanied by release of a large amount of heat, which ensures the occurrence of reaction (a). When the amount of methanol in the initial air-alcohol mixture is reduced, reaction (b) becomes predominant in the process, which causes the temperature to rise above the optimal level if the abstraction of heat is not adequate, hence, leads to a sharp increase in the chemical losses of methanol.

The yield of formaldehyde depends on the methanol-to-oxygen ratio. In commercial production the optimal molar ratio of methanol to oxygen ranges roughly between 2.2 and 2.5. If the contact time is not sufficient, that is if the volume velocity is high, the overall conversion of methanol decreases and so does the formaldehyde yield. At a low volume velocity, the conversion is more complete, which, in turn, increases the chemical losses in the form of carbon oxides (CO and CO_2). The optimal contact time corresponds to a volume velocity of 8000 h^{-1}.

The commercially used contact represents silver applied on pumice or another porous support. The various impurities present in the support may accelerate undesired side reactions. In particular, iron promotes the reaction of methanol dehydrogenation all the way to formation of carbon black. Therefore, the support has to be purified to remove the impurities adversely affecting the contact properties.

In carrying out this work the process parameters are to be varied within the following ranges: temperature—650 to 700°C, volume velocity—6000 to 9000 h^{-1}, and methanol-to-oxygen ratio—2.2 to 2.5.

This work involves studying heterogeneous catalytic conversion of methanol to formaldehyde in a filtering catalyst bed under different operating conditions of the catalytic reactor.

Experimental Setup and Procedure

The experimental setup for heterogeneous catalytic conversion of methanol to formaldehyde is shown schematically in Fig. 57. An amount of 30 to 50 cm³ of methanol are heated in the alcohol evaporator *5* to 43-45°C (with a high degree of accuracy) with the aid of a thermostat *7*. Air is fed by an air blower *1* at a rate of 0.5 to 2 dm³/min and bubbles through methanol in the alcohol evaporator.
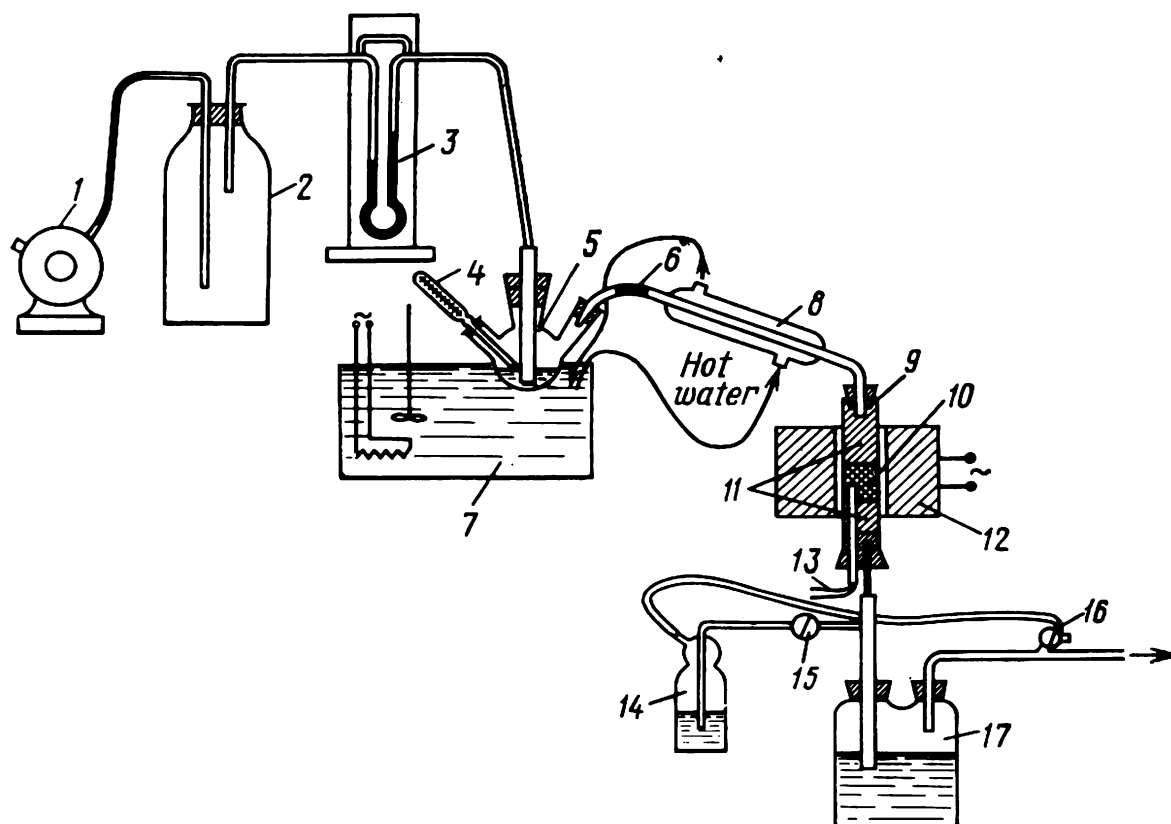
Fig. 57. Experimental setup for catalytic conversion of methanol to formaldehyde

1—air blower; *2*—surge bottle; *3*—rheometer; *4*—thermometer; *5*—alcohol evaporator; *6*—flame trap; *7*—thermostat; *8*—alcohol superheater; *9*—catalytic reactor; *10*—catalyst bed; *11*—quartz layer; *12*—furnace; *13*—thermocouple; *14*—Drexel bottle; *15, 16*—cocks; *17*—flask with water

The resulting air-alcohol mixture passes through the flame trap *6*, alcohol superheater *8*, and enters the catalytic reactor *9* (quartz tube; catalyst—silver on pumice) heated to 500-670°C with the aid of the furnace *12*. As the air-alcohol mixture passes through the silver catalyst bed *10* (sandwiched between quartz layers *11*), methanol undergoes conversion at a given temperature.

The condensing reaction products (the resulting formaldehyde as well as the unreacted methanol and reaction water) are absorbed in a flask *17* with water, while the uncondensed gases (H_2, CO, CO_2, CH_4, O_2, N_2) are vented into the atmosphere after sampling. After the process parameters have attained the desired values, all of the

gas is passed by the cock *15* through the Drexel bottle *14* with water within a specified time interval. The resulting solution is analyzed for formaldehyde and methanol contents, after which the percentage conversion of methanol to formaldehyde is calculated.

B. INCOMPLETE OXIDATION OF METHANE

The incomplete oxidation of methane to yield valuable oxygen-containing products is one of the most promising ways to utilize natural gas. At relatively low temperatures of methane oxidation, the following main reactions take place:

$$CH_4 + 2O_2 = 2H_2O + CO_2 + 802 \text{ kJ} \tag{a}$$

$$CH_4 + 1.5O_2 = 2H_2O + CO + 519 \text{ kJ} \tag{b}$$

$$CH_4 + O_2 \rightleftharpoons H_2O + CH_2O + 283 \text{ kJ} \tag{c}$$

$$CH_4 + 0.5O_2 \rightleftharpoons CH_3OH + 126 \text{ kJ} \tag{d}$$
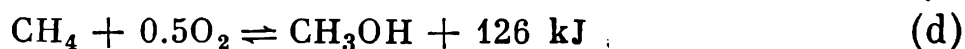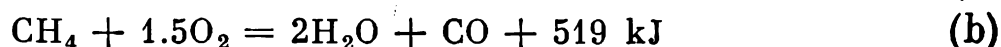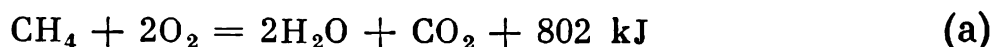
If the oxygen is in excess and the process is slow, the products CH_2O and CH_3OH may oxidize further:

$$CH_3OH + 0.5O_2 = CH_2O + H_2O + 156.5 \text{ kJ} \tag{e}$$

$$CH_2O + 0.5O_2 \rightleftharpoons CO + H_2O + 236 \text{ kJ} \tag{f}$$
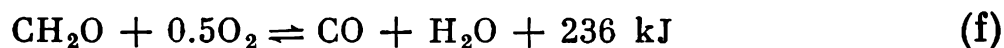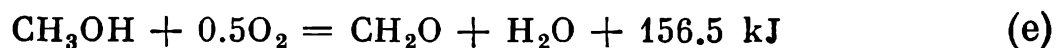
At the same time, the resulting formaldehyde may undergo thermal decomposition:

$$CH_2O \rightleftharpoons CO + H_2 - 5.4 \text{ kJ}$$

Initially, the methane oxidation process requires a great amount of activation energy, but then it proceeds at an increasing rate till formation of complete oxidation products (CO, CO_2, H_2O). What makes the methane oxidation reaction so special is that the methane molecule itself is relatively inert, which is particularly manifest if methane is compared with one of the intermediate products of its oxidation—formaldehyde. While the energy of the C—H bond in methane is 423 kJ, that in formaldehyde is 331 kJ, hence the much more pronounced reactivity of the latter. And this is precisely why the reaction is difficult to initiate and much easier to conduct once it has been initiated. There have been a great variety of hypotheses set forth concerning the mechanism of the reaction. Experiments suggest that the oxidation of methane involves a chain mechanism, proceeding via free radicals with degenerated branching, and is characterized by the presence of an induction period followed by extremely fast complex chemical reactions.

By mitigating the activation energy, catalysts make for a sharp decrease in the induction period and process temperature, selectively speeding up certain reactions, which enhances the yield of valuable products. Thus, the catalyst improves the selectivity of oxidation to the same extent as it lowers the process temperature. The most com-

mon of the homogeneous catalysts used in the process are nitrogen oxides and hydrogen chloride.

The best way to produce formaldehyde is through incomplete oxidation of methane at a temperature not lower than 600°C and at atmospheric pressure. Particular attention should be given to avoid thermal and oxidative decomposition of formaldehyde. This is achieved by sharp cooling (quenching) of the reaction products.

In homogeneous catalysis use is made of nitrogen oxides fed continuously into the catalysis zone. In this case, not only are nitrogen oxide catalysts expensive, but also the formaldehyde absorption system is more complicated, as compared with heterogeneous catalysis (which yields pure formaldehyde), and expensive facilities are additionally required to clean the effluent gases from nitrogen oxide, if they are going to be utilized. Besides, the apparatus and piping must be made of special steels or receive anticorrosive coatings.

This work deals with homogeneous catalysis with incomplete oxidation of methane in the porcelain packing bed. The parameters to be maintained in carrying out this work are as follows: temperature—650 to 750°C, and volume velocity—6000 to 9000 h^{-1}.

Experimental Setup and Procedure

The setup for incomplete oxidation of methane present in natural gas under conditions of homogeneous catalysis is illustrated in Fig. 58. The reactor *11* is a quartz tube 25 to 30 mm in diameter, packed to two thirds of its height with porcelain lumps *12* (3 to 5 mm in size). The reactor is provided with heating coils or placed in a furnace for heating to a temperature of 650-750°C.

After the reactor has been heated to the desired temperature (measured by a thermocouple *14*), nitrogen oxides are fed from a gas holder *3* through a flask *4* with water and a rheometer *5* into a mixer *6* wrapped in cloth or fine wire mesh, so that the oxide bubbles pass through the flask *4* at a rate of about a bubble every two seconds. The air blower *1* is switched on, and the required air flow rate is adjusted by means of a rheometer *5*. Then, natural gas or methane from a bottle *2* starts being fed. The flask *4* for natural gas (or methane) is charged with 30 to 50 cm^3 of a 3% acidulated KMnO$_4$ solution (to scrub the passing gas). The gas and air feed rates vary within 3 to 5 cm^3 per minute and must be such as to enable counting of bubbles in the flasks *4*. A mixture of natural gas and air, supplied in equal volumes, is not explosive.

Downstream of the mixer *6*, the mixture is humidified at a particular temperature in the humidifier *8* placed in a thermostat *10*, then flows through a flame trap *9* into a reactor *11*. The condensing reaction products, including formaldehyde, methanol, and reaction water, are absorbed in the Drexel bottle *15* with a premeasured amount of

water, while the uncondensed gases (H_2, CO, CO_2, C_n, H_{2n}, O_2, CH_4, N_2) are vented into the atmosphere after sampling.

After the process has been brought to the steady state, that is the desired ratio of starting components in the gas mixture and temperature in the reactor have been attained, the gas mixture is passed by a cock *16* through the Drexel bottle *15* with water over a preset period of time. After the experiment, the amount of the solution
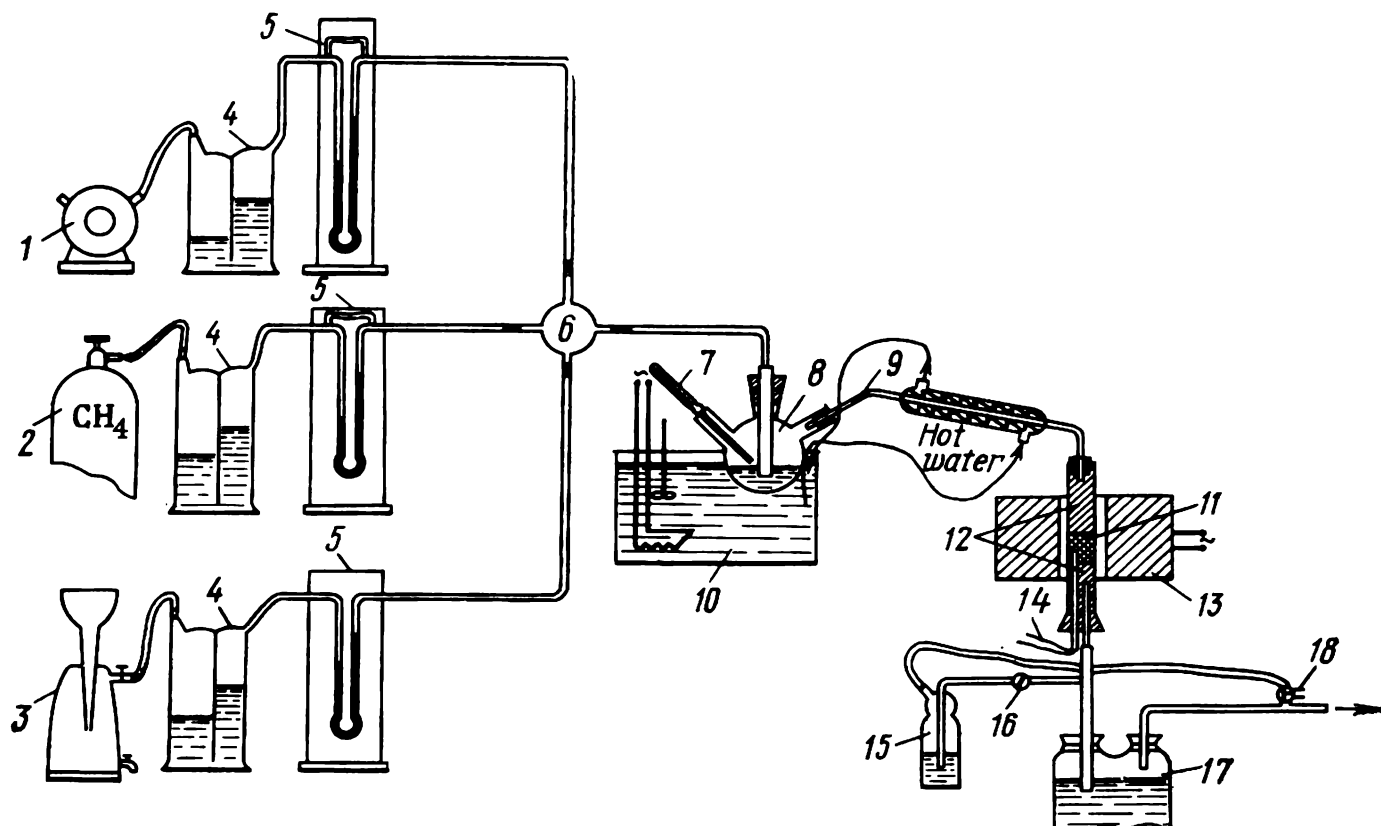
Fig. 58. Experimental setup for incomplete homogeneous oxidation of methane
1—air blower; *2*—bottle; *3*—gas holder; *4*—Tishchenko flask; *5*—rheometer; *6*—mixer; *7*—thermometer; *8*—humidifier; *9*—flame trap; *10*—thermostat; *11*—reactor; *12*—packing; *13*—furnace; *14*—thermocouple; *15*—Drexel bottle; *16, 18*—cocks; *17*—flask with water

formed in the Drexel bottle is measured, and the solution is analyzed for formaldehyde and methanol contents. The formaldehyde yield constitutes 2% of the total quantity of methane passed through the reactor.

Knowing the amounts of the resulting formaldehyde and methanol as well as the volume of the starting methane (natural gas), one can calculate the yield of valuable products of incomplete oxidation of methane.

Analysis of Uncondensed Gases. The determination of CO_2, unsaturated hydrocarbons, O_2, CO, H_2, and CH_4 is carried out using a ВТИ-2 gas analyzer, ЛТИ, a chromatograph, and other instruments (see Work 37, E).

C. OXIDATION OF DIMETHYL ETHER IN A FLUIDIZED CATALYST BED

The processes involved in heterogeneous catalysis in the presence of porous catalysts comprise several steps, including transfer of the gas (or liquid) phase onto the surface of catalyst grains from the flow and subsequent diffusion of the reagents inside the pores. The heat transfer follows a similar pattern. The use of a fluidized bed helps obviate most of the drawbacks inherent in fixed-bed catalytic reactors.

The vigorous motion of catalyst particles in a fluidized bed leads to intensive agitation of the gas phase with the result that the processes of mass and heat transfer become more intensive and the diffusion resistance decreases. A fluidized bed enables the use of small catalyst grains, which eliminates the internal diffusion resistance, whereby the process enters the kinetic range. As a result, the overall conversion of dimethyl ether to formaldehyde is enhanced although the latter decomposes to a greater extent in the free volume of the bed which is normally larger than in fixed-bed reactors.

Experimental Setup and Procedure

Dimethyl ether (2 to 4%) is formed as a by-product of methanol synthesis. Dimethyl ether is usually flared off. Its use as a source in the production of formaldehyde minimizes atmospheric pollution and is a major factor in designing a closed-loop almost waste-free process.

The oxidation of dimethyl ether proceeds according to the following equation:

$$CH_3OCH_3 + O_2 \rightleftharpoons 2CH_2O + H_2O + 285 \text{ kJ} \qquad (a)$$
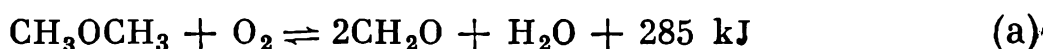
Concurrently, reactions of complete oxidation may take place

$$CH_3OCH_3 + 2O_2 \rightleftharpoons 2CO + 3H_2O + 760 \text{ kJ} \qquad (b)$$

$$CH_3OCH_3 + 3O_2 \rightleftharpoons 2CO_2 + 3H_2O + 1512 \text{ kJ} \qquad (c)$$
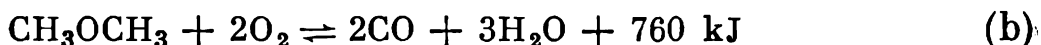
It is assumed that the reactions are based on a chain mechanism. Thermal decomposition of dimethyl ether yields methyl radicals initiating chain formation.

The experimental setup for oxidation of dimethyl ether is shown in Fig. 59. A reactor *11* is essentially a quartz tube 25 to 30 mm in diameter. It is provided with heating coils (or placed in an electric furnace) for maintaining its operating temperature within 450 to 550°C. After the reactor has been heated to the necessary temperature (measured by a thermocouple), an air blower *23* is switched on, and the air flow rate is adjusted by a rheometer. Then, dimethyl ether is fed from a bottle *1*, so that it passes together with air through manostats *2* and rheometers *4* and is mixed with air in a mixer *7*.

The ratio of dimethyl ether to air is maintained below the lower limit of the explosive range (3.5%) and normally equals 2.0 to 2.5% (monitored by the rheometers).

The ether-air mixture is fed into a temperature-controlled flask *9* with water, then, after it has been humidified, under a grid *16* of catalytic reactor *11* via a flame trap (not shown). The gas-distributing grid *16* is made of porous quartz. The catalytic reactor is thermally insulated by fireclay on which a nichrome wire is wound,
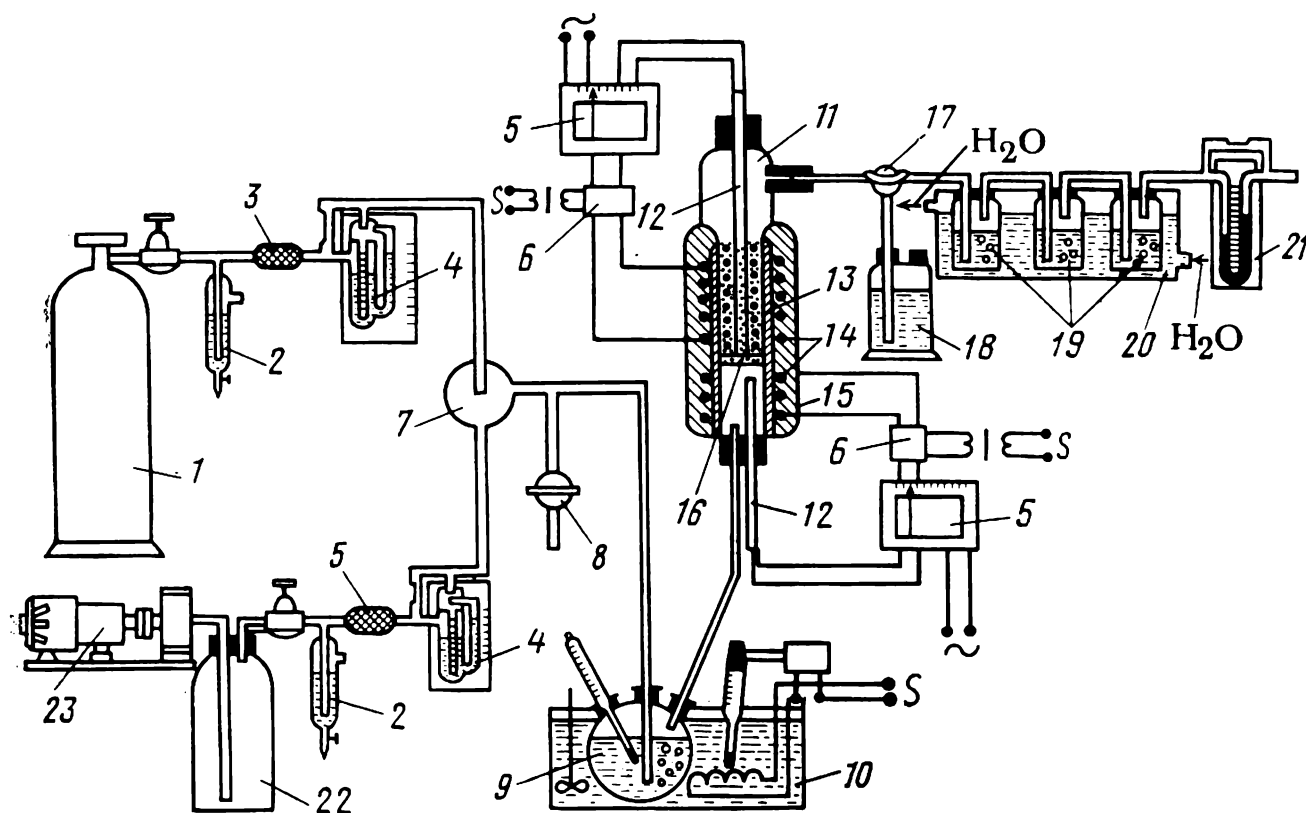
Fig. 59. Experimental setup for oxidation of dimethyl ether

1—bottle; *2*—manostat; *3*—flame trap; *4*, *21*—rheometers; *5*—potentiometer; *6*—relay; *8*, *17*—valves; *9*—humidifier; *10*—thermostat; *11*—reactor; *12*—thermocouples; *13*,*14* — coils; *15*—heat insulation; *16*—gas-distributing grid; *18*—flask with water; *19*—absorption flasks; *20*—cooling bath; *22*—surge bottle; *23*—air blower

connected via an autotransformer to an a-c source, for heating the ether-air mixture both at the reactor inlet and in the reaction zone.

To minimize the heat loss into the surrounding medium, the reactor is additionally enclosed in an asbestos jacket *13*, the temperatures under the grid of the reactor and in the reaction zone being measured by thermocouples connected to recording potentiometers *5*. The catalyst is tungsten trioxide WO_3 applied on a porous support with subsequent impregnation with phosphoric acid.

The conditions for creating a fluidized catalyst bed should be calculated in the following sequence:

1. Calculation of the Archimedes number:

$$Ar = \frac{gd^3}{v^2} \left(\frac{\rho_{cat} - \rho_{mix}}{\rho_{mix}} \right),$$ (2 55)

where d is the catalyst particle diameter, in m (if the catalyst particles vary greatly in size, d_{equiv}—equivalent particle diameter); ρ_{cat} is the apparent density of catalyst particles, in kg/m^3; ν is the viscosity of the gas mixture at the experimental temperature, in m^2/s; and ρ_{mix} is the density of the gas mixture at the experimental temperature, in kg/cm^3.

2. Calculation of the Reynolds number:

$$Re = \frac{Ar}{1400 + 5 \cdot 22 \sqrt{Ar}} \qquad (2.56)$$

3. Calculation of the flow rate relative to the overall cross-section of the reactor and corresponding to the initial weighing of the catalyst:

$$w_1 = Re \; \nu/d. \qquad (2.57)$$

4. Calculation of the working ether-air mixture flow rate w_w (with due account for the weighing factor n): $w_w = nw_1$. Normally, the weighing factor n varies from 1.5 to 2.5.

5. Calculation of the flow rate V_{mix} (V_{mix} depends on the cross sectional area S of the catalytic reactor):

$$V_{mix} = w_w S. \qquad (2.58)$$

6. Calculation of the flow rate of each individual component with due account for the component ratio (*ca.* 2.5% of dimethyl ether in the mixture). In this case, the flow rate is reduced to normal conditions.

To provide for a particular time τ_{cat} of contact between the ether-air mixture and the catalyst, a respective value of volume velocity V_{vol} (in cubic metres of gas per cubic metre per hour of catalyst) is assumed. Depending on the selected value of volume velocity, the reactor is charged with catalyst taken in a volume calculated using the formula

$$v_{cat} = V_{mix}/V_{vol}.$$

From the reactor, the reaction mixture is fed into a buffer vessel *18* (Fig. 59) communicating with the atmosphere. After the specified temperatures have been reached, the products are supplied into a system of series-connected absorption flasks *19* in which the condensed products (CH_2O, CH_3OH, CH_3COOH, $HCOOH$, etc.) are trapped. The uncondensed gases are sampled for analysis.

The air-tightness of the system is checked by means of a rheometer *21*. After the experiment, the amount of the solution formed in the absorption flasks (Drexel bottles) is measured, and the solution is analyzed for formaldehyde, methanol and acid ($HCOOH$, CH_3COOH) contents. Knowing the amount of the resulting formaldehyde, methanol, and acids, as well as the gas composition, one can calculate the yield of the end products.

Determination of Formaldehyde Content. Formaldehyde is analyzed using a 1 N solution of hydroxylamine hydrochloride. The reaction proceeds as follows:

$$H_2C = O + NH_2OH \cdot HCl \rightarrow H_2C = NOH + HCl + H_2O$$
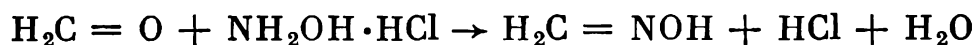
The released acid is titrated with 0.05 N KOH in the presence of a mixed methyl orange and indigo carmine indicator.

In an acidic medium this indicator turns violet, while in an alkaline medium it turns green. Before analysis, the amount of KOH spent in the titration of hydroxylamine hydrochloride is determined (neutral test).

To this end, 5 ml of the hydroxylamine hydrochloride solution are poured into a flask, then 25 ml of distilled water are added by pipette plus one or two drops of the indicator, and the mixture is titrated with 0.05 N KOH till the colouration becomes gray green. The liquid phase is analyzed similarly, except that 25 ml of the solution to be analyzed are used instead of distilled water.

The formaldehyde content is calculated using the formula

$$G = \frac{(a-b)\,\Phi q 100}{v}, \tag{2.59}$$

where G is the formaldehyde content in the solution, in % by weight; a is the amount of KOH, spent in the titration of the sample, in ml; b is the acidity of the hydroxylamine hydrochloride solution (in ml of the alkali spent in the neutral test); Φ is the titre of the KOH used; $q = 0.0015$ is the amount of formaldehyde (in g), equivalent to 1 ml of 0.05 N KOH; and v is the volume of the liquid phase.

Determination of Methanol Content. A 5-cm^3 sample of the solution is pipetted into a measuring flask having a capacity of 250 cm^3 plus 25 cm^3 of $K_2Cr_2O_7$, then 15 cm^3 of concentrated sulphuric acid are carefully added. The contents are stirred and allowed to stand for 10 to 15 minutes at room temperature. The resulting reaction is as follows:

$$CH_3OH + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow H_2CO_3 + K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O$$
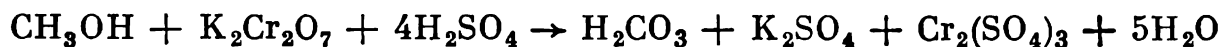
If the acid is taken in smaller amounts, the test results are irreproducible. The cooled solution is diluted to 250 cm^3 and stirred. An amount of 50 cm^3 of the diluted solution is pipetted for analysis into a conical flask, and approximately 5 cm^3 of 1.2 N KI are added. Then, the excess potassium dichromate decomposes in the following reaction:

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$
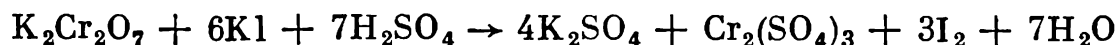
The resulting iodine is titrated with 0.1 N Na$_2$S$_2$O$_3$ in the presence of starch:

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$
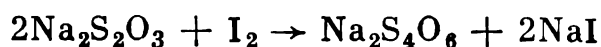
The distinct change in colouration clearly indicates the end of titration.

The methanol content is determined under industrial and laboratory conditions, in sufficiently concentrated solutions, using the Auerbach and Dittmar tables (given in the appendix to State Standard GOST 1625-61 "Commercial-Grade Formalin") and the following formula:

$$\rho = 1 - (\rho_1 - \rho_2) = 1 + \rho_2 - \rho_1, \qquad (2.60)$$

where ρ is the density of methanol in the analyzed formalin solution; ρ_1 is the density of the solution containing formaldehyde in an amount determined from Eq. (2.59) and is found in the Auerbach table (density of an aqueous solution of formalin at 15°C); and ρ_2 is the density of the analyzed formalin, determined with the aid of a densimeter at 15°C.

The percentage content of methanol in the analyzed formalin is determined from the density ρ and Dittmar table (density of an aqueous solution of methanol at 15.56°C). Since this experiment will not provide sufficient amounts of concentrated alcohol solutions, it will be best to resort to the methanol volume determination method based on potassium dichromate in solutions with a concentration of 1 to 0.1% by weight.

Calculation of the Alcohol Concentration. The weight percentage of methanol is calculated from the amount of potassium dichromate, spent in the oxidation, which is equal to

$$\frac{25}{10} \cdot 2 \cdot \frac{0.4}{1000} - e \frac{0.1}{1000},$$

where e is the amount of 0.1 N $Na_2S_2O_3$, spent in the titration of 50 cm³ of the solution.

To obtain the number of grammes of the methanol oxidized with potassium dichromate, one must divide the derived value by 6 (conversion of normality of potassium dichromate to molarity) and multiply the result by 32 (molecular weight of methanol). The result will be the number of grammes of methanol in $\frac{5}{10} \cdot 2$ g of the initial solution. The calculation based on 100 cm³ gives

$$\frac{\left(\dfrac{25}{10} \cdot 2 \cdot 0.4 - a 0.1 \right) 32 \cdot 100}{1000 \cdot 6 \cdot \dfrac{5}{10} \cdot 2} \cdot \frac{a}{100},$$

where a is the methanol, in g.

After the necessary transformations, the calculation formula takes the form

$$\text{wt.\% of methanol} = 0.05333 (20m - a), \qquad (2.61)$$

m being the correction factor to the titre of 0.4 N $K_2Cr_2O_7$.

In view of the fact that methanol is present in the solution together with formaldehyde which also reacts with potassium dichromate, the alcohol content must be calculated using the following formula taking into account the con-

centration of formaldehyde in the solution:

$$\text{wt.\% of methanol} = 0.05333 \,(20m - 13.33b - a) \qquad (2.62)$$

where b is the amount of formaldehyde, present in 100 cm³ of the solution, in g.

Knowing the amount of the passed natural gas (n), formaldehyde content (b), and that of methanol (a) in grammes in 100 cm³ of the solution, as well as the volume of the latter $(v$ in cm³), one can calculate the yield of valuable products (in g) per cubic metre of natural gas

$$g_{CH_2O} = bv1000/n100 = bv10/n \qquad (2.63)$$

and that of methanol

$$g_{CH_3OH} = av1000/n100 = av10/n. \qquad (2.64)$$

The chemical losses occurring in the process can be calculated from the results of gas analysis, using the Walker formula

$$\frac{CO_2 + CO + CH_4}{0.528N + 2(CH_4) - CO - 2(CO_2) - 2(O_2)}. \qquad (2.65)$$

After the experiment, it is necessary to draw a schematic of the setup, to explain the processes yielding formaldehyde, to tabulate the gas analysis results, to draw up a material balance with due account for chemical losses, and to plot curves representing the formaldehyde yield versus one of the following parameters: (a) type and amount of the contact: (b) temperature; (c) volume velocity; and (d) dimethyl ether-to-oxygen ratio in the starting mixture.

LITERATURE

Fluidized-Bed Catalysis, Mukhlyonov, I. P., Anokhin, V. N., Proskuryakov, V. A. *et al.*, Leningrad, 1978.

Production of Methanol and Formalin, Lender, Yu. V., Vedernikov, M. I., Rudoy, I. V. and Sukhov, V. P., Kiev, 1972, pp. 84-112.

Instructions to the Laboratory Work "Catalytic Processes of Formaldehyde Production"

Conversion of Methanol.

1. Switch on the heating after methanol has been poured into the alcohol evaporator.

2. Blow air through the superheater at 80 to 95°C and through the catalyst in the reactor at 400 to 750°C for at least 20 minutes.

3. Connect the alcohol evaporator to the superheater, and establish the experimental conditions according to the assignment, passing air through alcohol.

4. To avoid formation of explosive concentrations of methanol and the air-alcohol mixture, do not pass air through alcohol if its temperature is below 42°C. Let air into the alcohol evaporator only after the instructor has checked all joints for correct connection air-tightness.

5. When working with methanol, take the necessary precautions in handling inflammable and toxic liquids (see instructions).

5. Stop the experiment in the following sequence: after the air supply into the alcohol evaporator has been cut off, switch off all the heating devices and de-energize the air blower only after blowing air through the superheater and reactor.

Incomplete Oxidation of Methane and Dimethyl Ether.

1. As soon as the specified temperature is reached in the reactor, switch on the air blower and adjust the air flow using the rheometer. Start feeding natural gas and nitrogen oxides. Feed the mixture into the furnace after the necessary ratio of starting substances has been attained.

2. Carefully watch the instrument readings during the experiment and make sure that the system is airtight without any leakage of natural gas, ether, and admission of air.

3. Stop the experiment in the following sequence: (a) switch off all heating devices and de-energize the blower after blowing air through the system; (b) cut off the supply of natural gas from the bottle and that of nitrogen oxides from the gas holder.

LABORATORY WORK 20. ESTERIFICATION OF ALCOHOLS WITH CARBOXYLIC ACIDS

One of the promising trends in modern organic synthesis is the production of nonionic surfactants by esterification of polyalcohols with carboxylic acids, which are widely used as detergents, wetting agents, emulsifiers, dispersants, flotation agents and extensively applied in the petroleum, textile, ore-dressing, metal working and other industries.

Esterification is essentially a reaction of condensation of alcohols and acids (or acid anhydrides), yielding an ester and water:

$$RCOOH + R'OH \rightarrow RCOOR' + H_2O$$
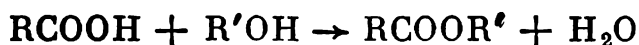
where R and R' stand for alkyl, aryl or aralkyl radicals. Reactions involving di- and polyhydric alcohols may yield partial and neutral esters:

$$
\begin{array}{ccccccc}
CH_2OH & & CH_2OCOR & & CH_2OCOR & & CH_2OCOR \\
| & \xrightarrow{RCOOH} & | & \xrightarrow{RCOOH} & | & \xrightarrow{RCOOH} & | \\
CHOH & + \; \rightleftarrows & CHOH & + \; \rightleftarrows & CHOH & + \; \rightleftarrows & CHOCOR \\
| & & | & & | & & | \\
CH_2OH & & CH_2OH & & CH_2OCOR & & CH_2OCOR \\
& & \text{monoester} & & \text{diester} & & \text{neutral ester}
\end{array}
$$
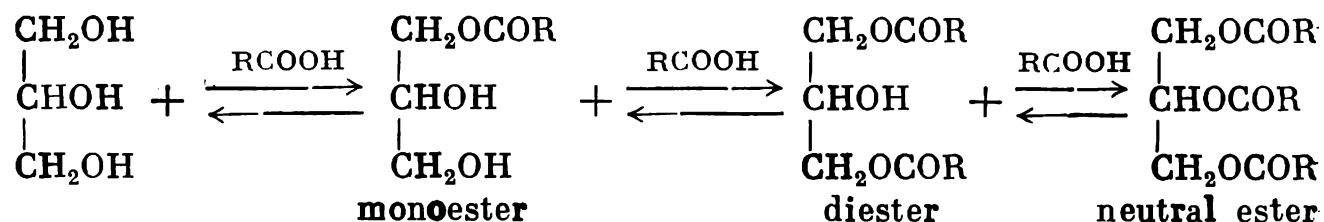
If the acid and alcohol belong to bifunctional compounds, the process yields high-molecular substances (polyesters):

$$HOOC-(CH_2)_4-COOH + HO-(CH_2)_2-OH \xrightarrow{-H_2O} HOOC-(CH_2)_4-$$

$$-COO(CH_2)_2OH \xrightarrow{+HO(CH_2)_2OH} HO-(CH_2)_2OOC-(CH_2)_4COO(CH_2)_2-OH \ldots$$
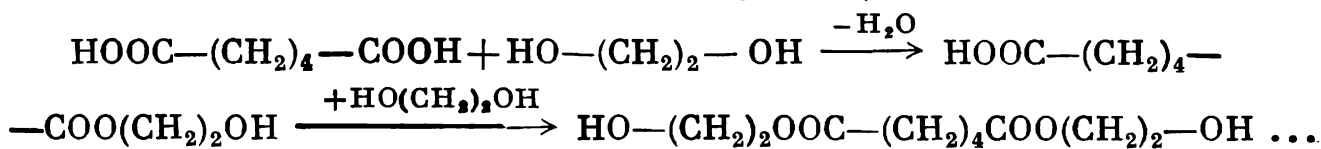
The esterification reaction is reversible. The back reaction is known as hydrolysis or saponification reaction.

The esterification of polyhydric alcohols with carboxylic acids is a complex consecutive reversible reaction proceeding in accordance with the second-order kinetic law (requiring a small amount of heat). It is also a homogeneous or heterogeneous catalytic liquid-phase

reaction. If one of the reaction products (water) is removed as it is being formed in the course of esterificaton, the equilibrium of the reaction shifts to the right, and the process becomes practically irreversible. In the general case, esterification follows a pattern common for complex reversible slightly endothermic reactions. The factors influencing the conversion, rate and selectivity of the process include the chemical nature of the raw material, reagent ratio, catalyst species, temperature, pressure, mixing intensity, and others. The starting substances used in esterification are mono- and polyhydric alcohols and acids of saturated, unsaturated and aromatic nature. The reaction rate and equilibrium position depend on the acid and alcohol structure. The reaction rate and equilibrium constant decrease from lower to higher and from primary to tertiary alcohols.

Changes in the molar ratio between the reagents affect the rate, equilibrium and selectivity of the process.

An equilibrium shift toward the end products may be attained by removing the resulting water from the reaction zone. The most complete dehydration is achieved by azeotropic distillation when a solvent forming an azeotropic mixture with water is introduced into the system.

An alternative way to remove the reaction water is blowing an inert gas, mostly nitrogen, through the reaction mixture or evacuation of the system.

The esterification reactions are conducted in the presence of catalysts. The most common catalysts include sulphuric and phosphoric acids, dry hydrogen chloride, aromatic sulpho acids, zinc oxide, and alkalis. In the case of acid catalysis, the proton interacting with the acid reagent yields an intermediate ion, and a substantial positive charge appears as a result of polarization of the bonds at the carbon atom of the carbonyl group. The reaction that follows is a nucleophilic attack of this complex by the alcohol molecule with subsequent detachment of water:
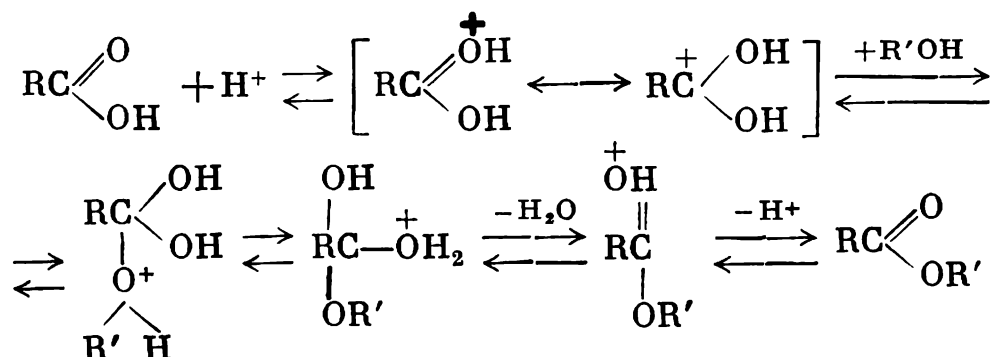
All steps of the process are reversible, and if their sequence is reversed, the result is ester hydrolysis (or alcoholysis if alcohol is used instead of water).

Extensive use has been made in recent years of catalysis by ionites (ion-exchange resins) of acidic or basic nature. The main advantages of ionites include the ease with which they can be separated from the reaction mixture, their long life, mildness and selectivity of action, and the fact that they do not cause gumming of the products and corrosion of the reactor metal.

The esterification rate increases and the equilibrium shift to the right becomes more pronounced with increasing temperature, since esterification belongs to reversible endothermic reactions. However, in selecting the optimal temperature, it should be borne in mind that a rise in temperature also speeds up side reactions (resinification, etc.).

By reducing pressure one can remove the reaction water more easily, thus increasing the ester yield. At the same time, the side reactions of polymerization and polycondensation (resinification) are inhibited since they are reversible and involve a reduction in volume (the equilibrium shifts markedly toward the starting substances).

The reaction time determines the attainment of equilibrium (or conversion of the starting substances), composition of the products, and the course of side reactions. A long time of residence of the starting substances in the reaction zone reduces the ester yield.

Alcohols and acids may dissolve in one another, but they also may form a heterogeneous system, which is why in the former case esterification is considered to be a homogeneous process, while in the latter, a heterogeneous one. The esterification rate is to a great extent dependent on the mixing intensity. Higher acids and alcohols are usually viscous liquids. Therefore, intensive mixing is conducive to a better distribution of the substances throughout the reaction volume (homogeneous process) or extends the area of phase-to-phase transfer (heterogeneous process).

The tasks to be performed in this work include studying multiple-factor processes; calculating the existing system of process parameters as well as kinetic constants, mass transfer data, etc., on the basis of material balances and analysis of the raw materials and products; summarizing and interpreting the results.

Experimental Design. The design of an experiment is aimed at defining the combination of process-related factors, which enables optimization of certain parameters (cost, conversion, yield, etc.). The associated studies are carried out by the multiple-factor experiment design method with statistical processing of the derived data. Adopted as the basis is the full factorial experiment (FFE) with a design of the 2^n type, n being the number of variable factors. The latter include such variables as X_1—temperature, °C; X_2—molar acid-to-alcohol ratio; X_3—catalyst concentration, % by weight; and X_4—catalyst type.

As the optimization parameters (response) are selected the following variables: Y_1—acid conversion; Y_2—alcohol conversion; Y_3—ester yield, %; and Y_4—reactor intensity.

To convert natural variables X_i to coded ones x_i, one must fill the following two-level factor coding table (the reference level and variation ranges are specified by the instructor):

Variation range and factor levels	X_1	X_2	X_3
Reference level, X_0 Variation range, ΔX Lower level Upper level Code	 x_1	 x_2	 x_3

The relationship between the coded and natural values of a factor is given by the following linear transformation:

$$x_i = (X_i - X_0)/\Delta X. \qquad (2.66)$$

Then, a design matrix of an experiment of type 2^2 or 2^3 is prepared as follows:

Design Matrix of FFE of Type 2^2

Experi-ment	x_1	x_2	$x_1 x_2$	Parallel experiments		$\overline{Y}_u = \dfrac{Y_{u_1} + Y_{u_2}}{2}$
				Y_{u_1}	Y_{u_2}	
1	-1	-1	$+1$			
2	$+1$	-1	-1			
3	-1	$+1$	-1			
4	$+1$	$+1$	$+1$			

Design Matrix of FFE of Type 2^3

Exper-iment	x_1	x_2	x_3	$x_1 x_2$	$x_1 x_3$	$x_2 x_3$	$x_1 x_2 x_3$	Parallel experiments		$\overline{Y}_u = \dfrac{Y_{u_1} + Y_{u_2}}{2}$
								Y_{u_1}	Y_{u_2}	
1	-1	-1	-1	$+1$	$+1$	$+1$	-1			
2	$+1$	-1	-1	-1	-1	$+1$	$+1$			
3	-1	$+1$	-1	-1	$+1$	-1	$+1$			
4	$+1$	$+1$	-1	$+1$	-1	-1	-1			
5	-1	-1	$+1$	$+1$	-1	-1	$+1$			
6	$+1$	-1	$+1$	-1	$+1$	-1	-1			
7	-1	$+1$	$+1$	-1	-1	$+1$	-1			
8	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$			

After the experimental design has been realized, the response function is approximated by a linear model (first-order polynomial):

$$\widehat{Y}_i = B_0 + B_1 x_1 + B_2 x_2 + B_3 x_3, \quad \text{where} \quad i = \overline{1.4.}$$

If the linear model is inadequate, the following pure quadratic equation is used:

$$\widehat{Y}_i = B_0 + B_1 x_1 + B_2 x_2 + B_3 x_3 + B_{12} x_1 x_2 + B_{13} x_1 x_3 +$$
$$+ B_{23} x_2 x_3 + B_{123} x_1 x_2 x_3.$$

If all coefficients in the equation are significant, the number of experiments will equal that of coefficients in the equation, and the adequacy of the model can be verified only by conducting additional experiments (all factors being at the reference level). If the incomplete quadratic model is inadequate or the effect of quadratic terms is significant, a quadratic equation must be used for approximation. To define the coefficients of the second-degree polynomial, one may resort to orthogonal central composite design (CCD).

An adequate model is used to select the method of motion over a gradient toward the optimum region. To define the optimal conditions of the process, the second-degree equation must be analyzed for an extremum.

Experimental Setup and Procedure

The esterification of glycols and glycerine with carboxylic and naphthenic acids is investigated using the setup of Fig. 60. The starting materials and catalyst are charged into the reactor *3* through a nipple *7* which is then capped by a nut *8* with a gasket. The reactor incorporates an agitator and is provided with heating coils. A holder made in the reactor receives a contact thermometer *4* associated with a temperature controller *2*, and the mixture is heated with the aid of the heating coils *10* with the reagents being vigorously stirred by the agitator *5* driven by an electric motor *6*. The reaction water vapours enter a condenser *11*. The condensate is trapped in a graduated cylinder *12*. The cock *9* is used to take samples and to discharge the product.

The content of unconverted acids in the initial and reaction mixtures is determined by titration of a weighed amount of the mixture with an alcohol solution of an alkali. The free acid content is estimated in terms of the acid number (a.n.) which corresponds to the number of milligrammes of KOH necessary to neutralize the free acids present in 1 g of the product. The theoretical acid number is the number of milligrammes of KOH, corresponding to 1 g of a

100% acid, and is calculated from the stoichiometric equation

$$RCOOH + KOH \rightleftharpoons RCOOK + H_2O$$
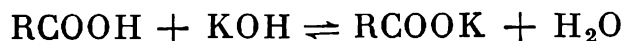
where R stands for alkyl, aryl or aralkyl radicals. To determine the acid number, 20 ml of 96% ethanol are poured into a conical flask, heated to boiling on a water bath with a reflux air condenser, and neutralized with several drops of 0.1 N KOH in the presence of phenolphthalein. Another flask is charged with a weighed amount of the product (about 1 g), filled with boiling neutralized alcohol,
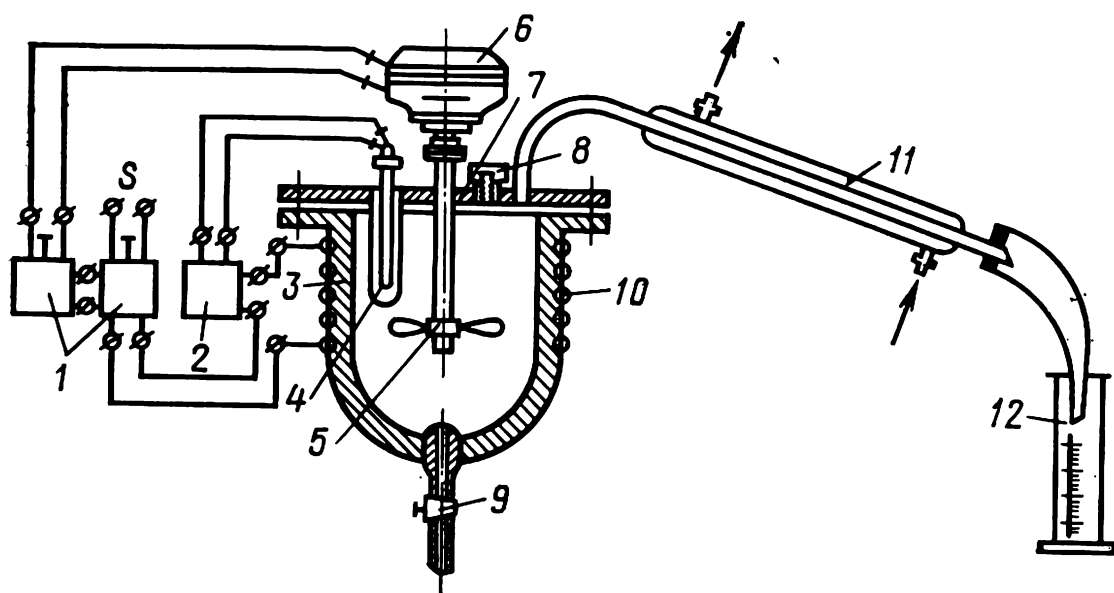
g. 60. Experimental setup for synthesis of esters

1—laboratory autotransformer; *2*—temperature controller; *3*—reactor; *4*—contact thermometer; *5*—agitator; *6*—electric motor; *7*—charging nipple; *8*—nut with a gasket; *9*—cock; *10*—heating coil; *11*—condenser; *12*—graduated cylinder

and the product is dissolved under heating with a reflux condenser. The hot mixture is titrated with a 0.1 N alcohol solution of KOH in the presence of phenolphthalein till it acquires a pink colour persistent during shaking. The acid number is calculated using the formula

$$\text{a.n.} = vT1000/a, \tag{2.67}$$

where v is the amount of 0.1 N KOH, spent in the titration of the product, in cm^3; T is the titre of the alcohol solution of KOH, in g/cm^3; and a is the weighed amount of the product, in g.

The *material balance* of the process is drawn up from analysis of the reaction mixture and the results of weighing the starting materials and products, as follows:

In			Out		
Starting materials	Weight, g	%	Products	Weight, g	%
Stearic acid Ethylene glycol	g_a g_g		Ester Unconverted acid Unconverted glycol Water Losses	g_e $g_{u.a.}$ $g_{u.g.}$ g_w g_l	
Total			Total		

The balance characteristics are calculated from the material balance data.

1. Acid conversion x_a

$$x_a = (g_a - g_{u.a.})/g_a. \qquad (2.68)$$

2. Glycol conversion x_g

$$x_g = (g_g - g_{u.g.})/g_g. \qquad (2.69)$$

3. Ester yield x_e

$$x_e = (g_e/g_{t.e.})\, 100\%, \qquad (2.70)$$

where $g_{t.e.}$ is the theoretical yield of ester, calculated from the material balance data and stoichiometric equation. In the case of monohydric alcohol,

$$g_{t.e.} = \frac{g_a \cdot \text{mol. weight of ester}}{\text{mol. weight of acid}}\, ; \qquad (2.71)$$

and in the case of polyhydric alcohol,

$$g_{t.e.} = \frac{g_a \cdot \text{mol. weight of ester}}{n \cdot \text{mol. weight of acid}}\, , \qquad (2.72)$$

n being the number of esterified OH groups.

4. Starting material consumption factors:

$$g_a/g_e \text{ t/t—acid}; \quad g_g/g_e \text{ t/t—glycol.}$$

Reactor intensity I:

$$I = g_e/V\tau \text{ g/(l·h)}, \qquad (2.73)$$

where V is the volume of the reaction mixture, in l; τ is the reaction time, h.

5. Calculation of $g_{u.a.}$, $g_{u.g.}$, and g_e from the results of reaction mixture analysis (see Example 1).

Example 1. The reactor is charged with 140 g of stearic acid and 15 g of ethylene glycol. An amount of 150 g of the reaction mixture with a.n. 19.75 is obtained. Calculate $g_{u.a.}$, $g_{u.g.}$, and g_e.

Solution. 1. Calculate $g_{u.a.}$:

$$G = \frac{19.75 \cdot 100}{197.5} = 10\%,$$

hence, in 150 g of the mixture, $g_{u.a.} = 150 \cdot 0.1 = 15$ g or $15/284 = 0.052$ mole, where 284 is the molecular weight of stearic acid.

To calculate the stearic acid concentration, one must know the volume v of the system.

2. Calculate the amount of converted acid:

$$140 - 15 = 125 \text{ g, or } 125/284 = 0.44 \text{ mole.}$$

3. Calculate the amount of converted glycol:

$$2StCOOH] + HO(CH_2)_2OH \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} (CH_2)_2(OOCSt)_2 + 2H_2O$$
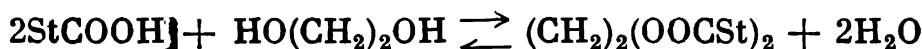
$0.22 \cdot 62 = 13.64$ g, where 62 is the molecular weight of glycol. Then, $g_{u.g.} = 15 - 13.64 = 1.36$ g or $1.36/62 = 0.022$ mole.

4. Calculate the amount of the resulting ester:

$$g_e = 0.22 \cdot 594 = 130.68 \text{ g,}$$

594 being the molecular weight of ester.

The *mathematical description* (model) of the process, based on coded factors, takes the form of a polynomial of a particular degree:

$$\hat{Y}_n = B_0 + B_1x_1 + B_2x_2 + \ldots + B_nx_n + \ldots + B_{12}x_1x_2 +$$
$$+ B_{n-1}, nx_{n-1}x_n + \ldots + B_{11}x_1^2 + \ldots + B_{nn}x_n^2 + \ldots$$

The statistical analysis of the results boils down to verification of the reproducibility of the experimental results, determination of the coefficients in this equation, verification of adequacy of the linear model, and evaluation of the significance of the equation coefficients.

Example 2. Give a mathematical description of the process, based on the data from the following table:

Exper-iment	x_1	x_2	x_1x_2	Results of parallel experiments		$\overline{Y}_u = \dfrac{Y_{u_1} + Y_{u_2}}{2}$	$(Y_{u_1} - Y_{u_2})^2$
				Y_{u_1}	Y_{u_2}		
1	-1	-1	$+1$	27	28	27.5	1
2	$+1$	-1	-1	15.9	17.1	16.5	1.44
3	-1	$+1$	-1	22.1	22.9	22.5	0.64
4	$+1$	$+1$	$+1$	13.4	13.6	13.5	0.04

Solution. 1. Check the equal accuracy of the results with reference to the Cochran number. To this end, find the variance of the results at each point of the design, using the formula

$$S_u^2 = (Y_{u_1} - Y_{u_2})^2/2, \tag{2.74}$$

$$S_1^2 = (27-28)^2/2 = 0.50; \quad S_2^2 = (15.9-17.1)^2/2 = 0.72;$$

$$S_3^2 = (22.1-22.9)^2/2 = 0.32; \quad S_4^2 = (13.4-13.6)^2/2 = 0.02.$$

The process is considered to be reproducible if the following inequality is satisfied:

$$Y = \frac{S_{u\,max}^2}{\sum\limits_{u=1}^{n} S_u^2} \leqslant Y\,(0.05;\ f_n;\ f_u), \tag{2.75}$$

$$Y = \frac{0.72}{0.50+0.72+0.32+0.02} = 0.4615 < Y\,(0.05;\ 4.1) = 0.9065,$$

where $Y\,(0.05;\ 4.1) = 0.9065$ is the tabulated Cochran number at a 5% level of significance and degrees of freedom $f_n = 4$ and $f_u = m - 1 = 1$ (see Appendix, Table 4).

The reproducibility variance is

$$S_y^2 = \frac{\sum\limits_{u=1}^{n} S_u^2}{n} = \frac{0.50+0.72+0.32+0.02}{4} = 0.39.$$

2. Calculate the coefficients of the equation:

$$B_0 = \frac{\sum\limits_{u=1}^{n} \overline{Y}_u}{n} = \frac{27.5+16.5+22.5+13.5}{4} = 20;$$

$$B_i = \frac{\sum\limits_{u=1}^{n} x_{iu}\overline{Y}_u}{n};$$

$$B_{ij} = \frac{\sum\limits_{u=1}^{n} x_{iu}x_{ju}\overline{Y}_u}{n};$$

$$B_1 = \frac{-27.5+16.5-22.5+13.5}{4} = -5;$$

$$B_2 = \frac{-27.5-16.5+22.5+13.5}{4} = -2;$$

$$B_{12} = \frac{+27.5-16.5-22.5+13.5}{4} = 0.5.$$

3. Verify the significance of the equation coefficients with reference to the Student *t*-test. A coefficient is said to be significant if the following inequality is satisfied:

$$|B_i| \geqslant t\,(0.05;\ f_y) \frac{S_y}{\sqrt{n}}, \tag{2.76}$$

where t $(0.05; f_y)$ is the Student t-test at 5% level of significance, and degrees of freedom $f_y = 4$, $t = 2.7764$ (see Appendix, Table 5).

$$B_0 = 20 > 2.7764 \frac{\sqrt{0.39}}{4} = 0.8669; \quad B_1 = 5 > 0.8669;$$

$$B_2 = 2 > 0.8669; \quad B_{12} = 0.5 < 0.8669.$$

All coefficients are significant except for B_{12}. This means that the factor in question does not affect Y within the selected variation range. Thus, the linear model of the process is $Y = 20 - 5x_1 - 2x_2$.

4. Verify the adequacy of the linear model with reference to Fisher's variance ratio. The model is adequate if the following inequality is satisfied:

$$F = \frac{S^2_{ad}}{S^2_y} \leqslant F(0.05; \quad f_{ad}; \quad f_y), \tag{2.77}$$

where F $(0.05; f_{ad}; f_y)$ is the tabulated Fisher's variance ratio at 5% level of significance and degrees of freedom $f_{ad} = n - k - 1$ and $f_y = 4$.

Calculate the adequacy variance

$$S^2_{ad} = \frac{\sum\limits_{u=1}^{n'} (\overline{Y}_u - Y_u)^2}{n - k - 1}; \tag{2.78}$$

Y_u is the calculated value of the response in the uth experiment.

$$Y_{1c} = 20 - 5(-1) - 2(-1) = 27, \quad (\overline{Y}_1 - Y_{1c})^2 = 0.25$$

$$Y_{2c} = 20 - 5(+1) - 2(-1) = 17, \quad (\overline{Y}_2 - Y_{2c})^2 = 0.25$$

$$Y_{3c} = 20 - 5(-1) - 2(+1) = 23, \quad (\overline{Y}_3 - Y_{3c})^2 = 0.25$$

$$\overline{Y}_{4c} = 20 - 5(+1) - 2(+1) = 13, \quad (\overline{Y}_4 - Y_{4c})^2 = 0.25$$

$$\sum = 1.00$$

$F = 1/0.39 = 2.564 < F (0.05; 1; 4) = 7.7086$ (see Appendix, Table 6). The model is adequate.

The derived model, if adequate to the experimental data, is analyzed depending on the assignment: it can be used to define the value of the response at particular values of the factors lying within the examined range; the model can also be analyzed at an extremum, and the maximum value of the response can be defined.

Example 3. The following equation has been derived:

$$y = 20 - 5x_1 - 2x_2, \tag{1}$$

where x_1 is temperature, in °C, and x_2 is the catalyst concentration, in %.

The basic level for x_1 is 300°C.

The variation range is 50°C.

The basic level for x_2 is 1.1%.

The variation range is 0.2%.

Calculate the acid conversion y at 320°C and a catalyst concentration of 1.1%.

Solution. Code the factors

$$x_1 = \frac{320 - 300}{50} = 0.4; \quad x_2 = \frac{1.1 - 1}{0.2} = 0.5.$$

2. Substitute x_1 and x_2 into Eq. (1) to obtain the acid conversion:

$$y = 20 - 5 \cdot 0.4 - 2 \cdot 0.5 = 17.$$

Example 4. Define the optimal conditions of a process described by the equation

$$y = 20 - 5x_1 - 2x_2 + x_1x_2. \qquad (2)$$

Solution 1. Bring the equation of the model to a canonical form. Differentiate Eq. (1) with respect to x_1 to obtain the coefficients of an extremal point:

$$\partial y/\partial x_1 = -5 + x_2 = 0, \text{ hence } x_{2C} = 5.$$

$$\partial y/\partial x_2 = -2 + x_1 = 0, \text{ hence } x_{1C} = 2.$$

Substitute these values into Eq. (2) to have

$$y_c = 20 - 5 \cdot 2 - 2 \cdot 5 + 2 \cdot 5 = 10.$$

2. Introduce new coordinate axes:

$$\alpha = -(B_{11} + B_{22}) = 0; \quad \beta = B_{11}B_{22} - 0.25B_{12}^2 = -0.25 \cdot 1^2 = -0.25.$$

Substitute these values into the equation for finding the roots of the characteristic equation

$$\theta_1 \text{ and } \theta_2; \quad \theta^2 + \alpha\theta + \beta = 0; \quad \theta^2 - 0.25 = 0;$$

$$\theta_1 = 0.5; \quad \theta_2 = -0.5.$$

Then, the direction cosines will be defined from the expressions

$$\frac{m_i}{l_i} = \frac{2(\theta_1 - B_{11})}{B_{12}}; \qquad l_i = m_i = \frac{1}{\sqrt{1 + (m_i/l_i)^2}}; \qquad (2.79)$$

$$\frac{m_1}{l_1} = \frac{2 \cdot 0.5}{1} = 1; \qquad l_1 = m_1 = \frac{1}{1 + 1^2} = 0.7071;$$

$$\frac{m_2}{l_2} = \frac{2 \cdot (-0.5)}{1} = -1; \qquad l_2 = 0.7071; \quad m_2 = -0.7071.$$

Finally,

$$y - y_c = \sum_{i=1}^{k} \theta_i z_c^2 + \sum_{g=2H}^{k} c_j z_j \quad \text{or} \quad y - 10 = 0.5z_1^2 - 0.5z_2^2,$$

where $z_1 = l_1(x_1 - x_{1c}) + m_1(x_2 - x_{2c}) = 0.7071(x_1 - 2) + 0.7071(x_2 - 5);$

$z_2 = l_2(x_1 - x_{1c}) - m_2(x_2 - x_{2c}) = 0.7071(x_1 - 2) - 0.7071(x_2 - 5).$

Then, $x_1 = 0.7071z_1 + 0.7071z_2 + 2,$

$x_2 = 0.7071z_1 - 0.7071z_2 + 5.$

The canonical form of the second-degree equation makes it possible to classify the extremal point and the response surface. The coefficients θ_1 and θ_2 have dissimilar signs: θ_1 is positive, consequently, the yield $y - y_c$ increases along the z_1 axis on either side of the figure centre and decreases along the z_2 axis. The response surface is a hyperbolic paraboloid with its centre at the point $x_{1c} = 2$; $x_{2c} = 5$.

The kinetic study resides in determination of the type of the kinetic equation as well as the values of such kinetic constants as order, rate constant, activation order, and others. The mean esterification rate $\overline{W}_e$ can be calculated using the formula

$$\overline{W}_e = C_D/\tau, \qquad (2.80)$$

where C_D is the current ester concentration, in mole/l, and τ is time, in min. The concentration C_D can be expressed in terms of C_A which is the initial acid concentration: $C_D = C_{A_0}\alpha_A/2$, α_A being the acid conversion by instant τ. The factor 1/2 is introduced for glycol. The acid conversion x_A can be calculated from the formula

$$x_A = (C_{A_0} - C_A)/C_{A_0}, \qquad (2.81)$$

where C_A is the current acid concentration defined in terms of the acid number of the reaction mixture or the amount of released water (see p. 212), in mole/l.
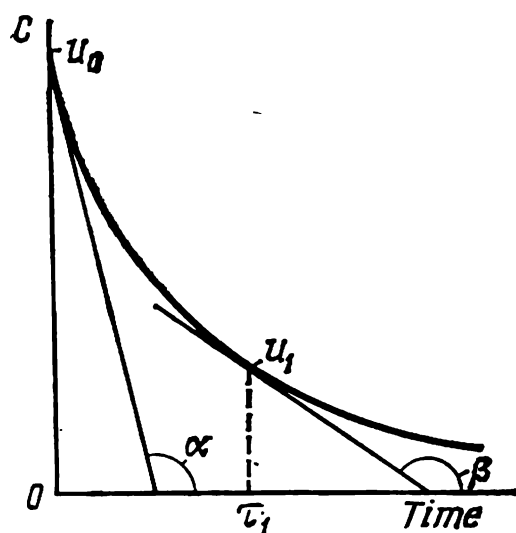
Fig. 61. Kinetic curve for determining the reaction rate
u_0—initial rate corresponding to τ_0;
u_1—rate corresponding to τ_1

The esterification rate is measured by the slope of the tangent to the kinetic curve (Fig. 61). To this end, the concentrations of the reagents or products are determined at definite time intervals (15 min), and a C-τ curve is plotted. The tangent is drawn to the point corresponding to a particular instant; the slope of the tangent to the abscissa corresponds to the reaction rate at a given point in time.

In determining the rate constant one should bear in mind that the esterification reactions are normally of the second order. To determine the reaction order use is made of graphic and calculation methods. If the initial acid and alcohol concentrations are equal, the esterification rate is given by the equation

$$dX/d\tau = k(a - X)^2, \qquad (2.82)$$

where a and X stand for the initial and final acid (or alcohol) concentrations, respectively, by instant τ. Integration gives an expression for calculating the reaction rate constant

$$k = \frac{1}{\tau} \frac{X}{a(a-X)} \qquad (2.83)$$

If the reagent concentrations are not equal, the rate of the second-order reaction is given by the equation

$$dX/d\tau = k(a - X)(b - X), \qquad (2.84)$$

where a and b are the initial reagent concentrations, in mole/l, and X is the final reagent concentration, in mole/l.

Integration of the rate equation gives the following expression for calculating k:

$$k = \frac{1}{\tau(a-b)} \ln \frac{b(a-X)}{a(b-X)}. \qquad (2.85)$$

To determine the rate constant, the reaction mixture is sampled at 10 min intervals, and the acid number is determined in the samples. The acid number is associated with the final acid concentration (unconverted acid). Having calculated the initial and final acid concentrations (see p. 214) at different τ and substituting them into the equation, one derives the rate constant values which must not differ more than within the experimental error. The experimental and calculation results are tabulated as follows:

Time, min	Acid number of the product	Number of moles of unconverted acid X	Number of moles of converted acid $a - X$	k, 1/mole·min	Standard deviation $(k - \bar{k})^2$
0 10 . . . 60					
				$\sum\limits_{i=1}^{n} k$	$\sum\limits_{i=1}^{n} (k - \bar{k})^2$

Six measurements are averaged to derive the mean value of the rate constant $\bar{k} = \sum\limits_{i=1}^{n} k/6$ and to determine the sum of standard deviations of each value of k from $\bar{k}$:

$$\sum\limits_{i=1}^{n} (k - \bar{k})^2.$$

The mean value is estimated with the aid of the τ criterion. To this end, the standard deviation $S = \sqrt{\sum\limits_{i=1}^{n} (k - \bar{k})^2/}$ /$(6 - 1)$ is calculated, then the confidence interval $\pm \Delta k$ is determined, that is the limits within which the true value of the constant $\pm \Delta k = \tau_{0.05} \dfrac{S}{\sqrt{6}}$ will lie with a certain probability. In statistical tables, the τ criterion for a 5% level of significance and the number of degrees of freedom $\nu = 6 - 1 = 5$ is $\tau_{0.05} = 2.57$; then, $\Delta k = 2.57 \cdot S/\sqrt{6} = 2.57/2.449S = 1.049S$.
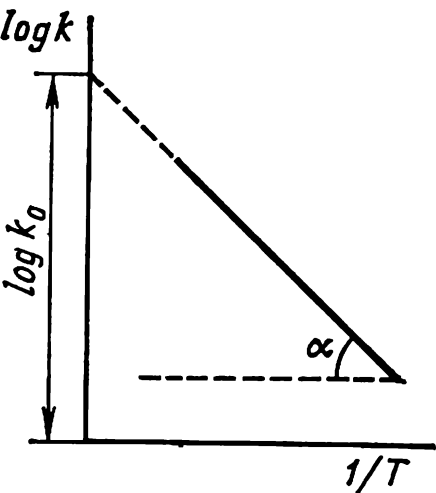
Fig. 62. Determination of E and k_0 ($E = 2.3R \tan \alpha$)

Hence, it can be asserted with a probability of 0.95 that $\bar{k}$ lies within $k \pm \Delta k$. The parameters E and k_0 can be defined graphically from the curve representing the reaction rate constant versus temperature:

$$\log k = \log k_0 - \frac{0.434E}{R} \cdot \frac{1}{T}.$$

The temperature dependence of the rate constant in coordinates $\log k - 1/T$ is linear (Fig. 62).

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Instructions to the Laboratory Work "Esterification of Alcohols with Carboxylic Acids"

1. Weigh the required amounts of the reagents and catalyst on a counter balance under an exhaust hood.

2. Melt stearic acid on a water bath, rub a weighed amount of the alkaline catalyst in a mortar and mix it with a weighed amount of alcohol.

3. Energize the heating coils and agitator of the reactor. Charge the acid and alcohol with the catalyst through a funnel at a temperature of not more than 80°C to avoid ejection of the product from the reactor. Preset the contact thermometer to the required temperature.

4. The onset of the reaction is marked by appearance of the first water drop. Monitor the process by measuring the amount of the released water or by determining the acid number of the reaction mass.

5. Take samples for determining the acid number through the discharge pipe of the reactor at predetermined time intervals and at the end of the process.

6. After the experiment, de-energize the heating coils and agitator of the reactor, then decant the end product into a weighed beaker.

7. After the analysis, decant the product into a special vessel and wash the container with hot water and soda. Discharge the washes into special bottles.

8. **To avoid being burnt by hot products, charge the starting materials, take the test samples, and discharge the products wearing gloves and goggles!**

Chapter 3

Automated and Computerized Apparatus

In recent years, analysis and design of industrial chemical processes, operation and control of chemical apparatus and process lines have undergone drastic changes. The high quality of products in intensive processes can be attained only if the process parameters are strictly maintained.

The advent and proliferation of computers have produced an indelible impact on the calculation of chemical processes. Computers have assumed the functions of design, simulation, control and management of chemical plants. The application of computers in systems for controlling the entire chemical process or an individual apparatus has made it possible to optimize chemical production.

Automation of reactor operation is one of the principal trends in chemical engineering. The most sophisticated automation involves the use of cybernetic devices which receive process data from measuring instruments and transducers, optimize the process variables, and preset them in each reactor and the process line as a whole with the aid of actuators. It has become standard practice in the chemical industry to use a reactor equipped with automatic instruments for measuring and recording process variables and interfaced with a computer which is fed with process data, optimizes the process variables, and controls the processes in the reactor through the medium of automatic actuators.

Most optimization techniques are based on the assumption that the mathematical model of the optimized system (i.e. the set of equations descriptive of the processes involved) is known. However, in solving the optimization problem one can use, in principle, the system to be optimized instead of a mathematical model, which requires that the system should be provided with appropriate instrumentation to evaluate its response to any variations in the input and determining variables, that is, in the final analysis, to derive respective mathematical relations. In this case, optimization calls for investigation of a great variety of operating conditions so that the best ones could be selected.

Therefore, it is extremely important to have a mathematical model of a process, which would suggest without interfering with the process itself, the decision to be taken in order to improve its

conditions. This means that the experiment at the process line is in fact substituted by experimentation with its model on a computer. A prerequisite for successful application of a mathematical model in solving the optimization problem is its adequacy, that is the model should simulate the system being optimized. To verify the adequacy of a mathematical model to a real process, one must compare the results of process variable measurements with the predictions provided by the model under identical conditions. Consequently, before embarking on optimization of a process, one must first of all make sure that the model is adequate. On the one hand, such a verification permits estimating the accuracy of the model, hence, determining its applicability to the optimization procedure. On the other hand, it can be used to eliminate the systematic errors occurring in modelling as a result of imprecise representation of some numerical parameters in the equations, particularly kinetic equation constants which cannot be defined exactly only from theoretical considerations or from the previous experience. In practice, one must reconcile oneself to the fact that no mathematical model can fully replace the system to be optimized and accept the necessity of using models that predict the behaviour of a real system only to a certain degree of approximation.

One and the same reactor can be simulated by several models differing in the number of variables involved, then, as a result of comparison of the mathematical modelling data with the variables of the real reactor, the adequate model can be chosen.

The mathematical models of reactors are based on the macrokinetic equations (1.12) through (1.17), the material balance being drawn up with respect to the basic starting substance A (see Eq. (1.17)) for a process of the A → D or A + B → D + E type, particularly if the component A is present in an amount insufficient in comparison with the stoichiometric ratio A : B.

All workable mathematical models of the processes occurring in reactors are based on idealized equations for plug-flow, perfect-mixing and intermediate conditions, the latter being represented by a diffusion model.

The *plug-flow model* of a continuous reaction is based on the reaction rate equation (1.17). For steady-state (stationary) conditions

$$u_A = -\frac{dC_A}{d\tau} \quad \text{or} \quad u_A = \frac{dx_A}{d\tau}. \tag{3.1}$$

Since $\tau = v/V_{mix} = H/w$, Eq. (3.1) takes the form

$$u_A = -V_{mix}(dC_A/dv), \tag{3.2}$$

or

$$u_A = -w(dC_A/dH), \tag{3.3}$$

where $u_A = k_1 \Delta C$ is the process rate (e.g., in the case of chemisorption of the component A with conversion to the product D) or $u_A = kC_{A^n}$ (e.g., in the case of an nth-order chemical reaction); τ is the process duration; v is the reactor volume; V_{mix} is the flow rate of the starting reaction mixture; H is the height (length) of the reaction volume through which the reaction mixture moves at the linear velocity w at the current basic starting substance concentration C_A; and x is the current percentage conversion of the substance A.

Accordingly, the characteristic equation of the plug-flow model corresponding to the steady-state conditions is expressed, for example, as follows:

$$-w\frac{dC_A}{dH} = u_A. \tag{3.4}$$

Under unsteady conditions, for a volume element of the reactor

$$\partial C_A/\partial\tau_{acc} + w\,(\partial C_A/\partial H) = -u_A, \tag{3.5}$$

where $\partial C_A/\partial\tau_{acc}$ is the rate of accumulation of the substance A in a volume element of the reactor within the accumulation time τ_{acc}.

If the process rate is expressed in terms of the percentage conversion x_A, taking into consideration Eq. (3.2) we have

$$V_{mix}C_A\,dx_A = u_A\,dv, \tag{3.6}$$

which gives the following characteristic equation for determining the process duration at a particular gas mixture volume V_{mix}:

$$\tau = \frac{v}{V_{mix}} = C_{A\bullet}\int_0^{x_A}\frac{dx_A}{u_A}, \tag{3.7}$$

where $C_{A\bullet}$ is the initial (specified) concentration of the reagent A.

The *perfect-mixing model* is based on kinetic equations similar to (1.12a, 1.13a, 1.26-1.28). The characteristic equation is written as

$$\tau = v/V_{mix} = C_{A_0}x_A/u_A. \tag{3.8}$$

The diffusion model takes into account the deviation of a real process in one phase of the system from plug-flow conditions by incorporating a term representing both convective (turbulent) mixing and molecular diffusion on the basis of the second Fick's law. The characteristic equation is

$$-w\,(\partial C_A/\partial H) + D_{eff}\,(\partial^2 C_A/\partial H^2) = u_A, \tag{3.9}$$

where D_{eff} is the effective diffusion coefficient taking into account both turbulent and molecular diffusions or, to be more precise, mixing of the reaction medium along the reactor axis.

The laboratory works included in this chapter deal with various processes: homogeneous and heterogeneous, low- and high-temperature, catalytic and noncatalytic, and with the reaction proceeding in the gas or liquid phase as well as on the surface of solid phases. In performing these works, students will have an opportunity to compare the performance of the basic types of reactors, batch and continuous, under perfect mixing, plug-flow and diffusion conditions, operating singly or in a cascade.

The mathematical description of processes has been intentionally simplified to enable students to synthesize an algorithm (solution program) necessary to derive the final equations in which the process variables are interrelated. As a rule, in each particular work students find the optimal value of a single process variable, although reactors are designed and installed so as to permit the optimal values of various variables to be determined separately or in combination.

LABORATORY WORK 21. AUTOMATED ABSORPTION PLANTS

I. DESCRIPTION, DESIGN, AND OPERATION

Absorption-desorption processes are widely used in many branches of the industry, particularly in the production of ammonia, soda, and sulphuric acid, in the petrochemical industry, in organic synthesis, and in the scrubbing of industrial gases to remove noxious impurities and dust. The currently employed types of absorbers can be classified as follows:

1. Packed towers in which gases are absorbed on the sprayed surface of the packing. The packing elements must have a developed surface. In most cases, these are in the form of steel or ceramic rings. Packed towers are simple in design and work stably if not intensively. They operate under conditions close to plug flow.

2. Towers or chambers in which the liquid is sprayed in a gas flow. In this case, the interfacial area equals that of the liquid drops. Difficulties in maintaining a steady mist of the liquid make the operation of such absorbers unstable.

3. Bubble columns with bubble-cap or sieve trays, in which the mass transfer takes place when gas is despersed through the liquid by bubbling, that is by passing gas bubbles through the liquid layer, with the gas being absorbed on the surface of the bubbles.

4. Froth apparatus which are the most intensively operating absorbers. Structurally, a froth apparatus represents a hollow chamber divided by one or several grids with the gas passing through them at such a velocity that the liquid on the grid becomes suspended in the gas flow because the forces of friction between the gas and liquid are in equilibrium with the weight of the latter. The result is a suspended layer of mobile froth in the form of rapidly moving

films, jets and drops of the liquid, which mix with the gas bubbles and jets as rapidly, whereby an extended surface of contact between the gas and liquid is formed and constantly renewed due to turbulization of the gas-liquid bed. Such apparatus operate under conditions close to perfect mixing.

As a consequence of intensive mixing, the froth bed is isothermal, which makes the process much easier to design and automate. The process of absorption under frothing conditions is highly intensive, which calls for a greater degree of automation as compared to extensive absorption.

It is precisely absorption with frothing that forms the principal subject matter of this work, its study involving the use of a computer. Also, to extend the scope of investigation and modelling, the absorption plant includes a packed column.

Automated absorption plants intended for industrial use (Fig. 63) are represented by two types of absorbers: a three-tray froth absorber *III* and a packed column *I*. The absorption plants are arranged in such a manner that both absorbers are integrated into a common process implemented within a closed-loop system and can operate both jointly and separately. They share the same systems for desorption, preparation and feed of the gas-air mixture, water, or aqueous solutions of ammonia.

The three-tray froth absorber as well as the packed column are the basic units of the absorption plants. The froth absorber is an apparatus with a rectangular cross-section ($S = 1$ dm^2). Water or an aqueous ammonia solution is fed onto the trays. The ammonia-air mixture is fed into the lower part of the apparatus and, as it passes through the tray perforations, either bubbles or froths the liquid, depending on its velocity. At the same time, the ammonia is partially absorbed by water. The absorber design, the system for controlling liquid flows with respect to the gas flow, and the possible range of variations in the gas velocity, spraying density and froth bed height permit the absorption process to be studied under a great variety of operating conditions of the absorber (Table 12).

The system of solenoid valves (Fig. 63, *61-76*) controlled from the keyboard of the control panel of the unit or the control computer as well as the system of control valves *104*, *3*, *5*, *6*, *7*, *73*, *17*, and *18* permit studying the effect of routing liquid flows with respect to the direction of gas flow and the spraying density of the absorption process. In this arrangement, the valves *61* through *63* are intended to control the liquid feed onto the third, second and first trays of the absorber. The valves *74* and *76*, *75* and *77*, and *73* control the switchover of the liquid flow from the third to second tray, from the second to first tray, and from the absorber out.

The valves *70* through *72* perform auxiliary functions. They must operate only before the system is started up and feed the liquid of

the same concentration to all solution analyzers (refractometers) at a time. Coincidence of the analyzer readings indicates that the data are valid.

The round packed column *I* having a diameter of 100 mm is divided into three sections between which samplers are arranged to
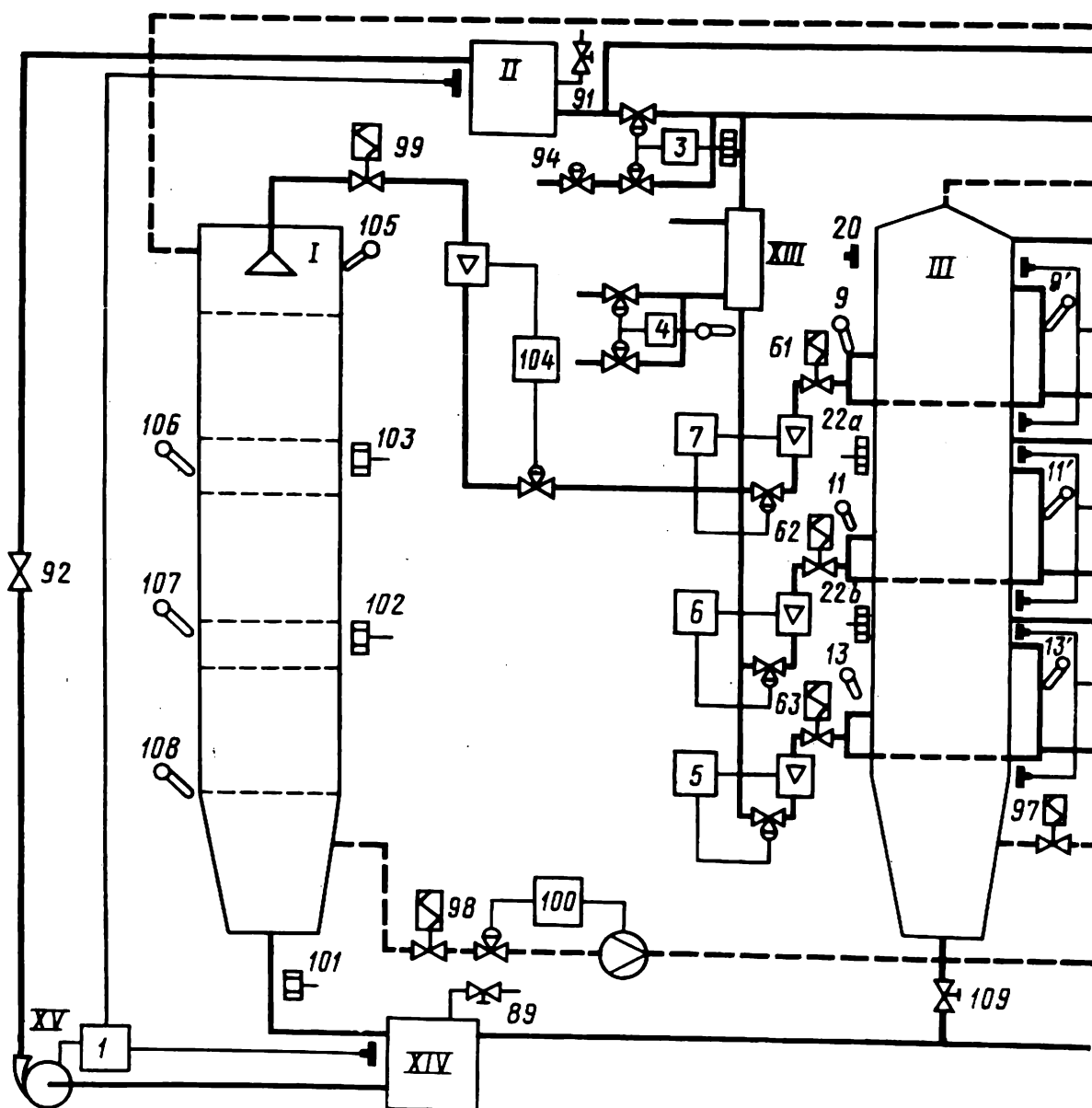
Fig. 63. Automated absorption plants:

I—packed column; *II*—overhead tank; *III*—froth absorber; *IV*—spray deflector; *V*—mixer; electric heater of the desorber; *XI*—gas blower; *XII*—electric gas-air mixture heater; *XIII*—

take gas and liquid samples for analysis. The liquid is supplied to the upper part of the column, while the ammonia-air mixture, into its bottom part. Each column section is provided with peepholes. Air from the gas blower *XI* is fed into the mixer *V*. Gaseous ammonia is also fed from the bottle *IX* through the Hofer valve and the pressure regulator *VI* into the mixer *V*. The amount of the ammonia fed into the mixer is controlled by a pneumatic valve *23* depending on

the specified concentration of the ammonia-air mixture. The latter then flows through a control valve *25* and an orifice plate into the absorbers downstream of the control valves *24*. The presence of two pneumatic control valves at this point permits regulating and stabilizing the temperature of the gas-air mixture.

VI—pressure regulator; *VII*—desorber; *VIII*—cooling coil; *IX*—ammonia bottle; *X*—liquid preheater; *XIV*—drain tank; *XV*—pump

Downstream of the apparatus, the gas reenters the gas circulation loop through the spray deflector *IV*. Part of gas flows into the desorber *VII* via the pneumatic control valve *23*. The rest enters the mixer in which the gas-air mixture is replenished either from the desorber or, if this is not sufficient for given operating conditions, from the ammonia bottle *IX*. The ammonia solution or water is fed from the overhead tank *II* or water line, respectively, to the inlet

of all three trays of the absorber and into the packed column.

The valves *3* and *4* together with the preheater *XIII* permit controlling the liquid concentration and temperature at the inlet of the absorbers. The liquid flows from the preheater in parallel onto the three trays of the absorber via the control valves *5*, *6*, *7* and induction flow meters as well as solenoid valves *61* through *63*. At the same time, the liquid may be fed into the upper portion of the packed column through the control valve *104* and an induction flow meter as well as through the solenoid valve *99*. The presence of the solenoid valves *61-63* and *70-76* makes it possible to create the necessary conditions for liquid flow on the absorber trays.

The solution from the absorber (end product) of the desired concentration flows through the control valves *73*, *17*, *18* and solenoid valves *77*, *76* into the drain tank *XIV*. The system for controlling the drain from each of the three trays of the froth absorber, consisting of a control valve, a differential pressure gauge, and an automatic pneumatic controller, allows the froth bed height to be controlled on each tray.

The concentration of ammonia solutions is monitored by refractometers *14*, *15*, and *16*, that is at the exit from each tray, and controlled by valves *3* and *79* at the point of entry into the absorber and at the exit from the desorber, respectively.

The ammonia solution is delivered from the drain tank *XIV* into the overhead tank *II* with the aid of the pump *XV* actuated by the level controller of the overhead tank *II*. It can be used for preparing weaker NH_4OH solutions to feed the absorber (if it does not run on pure water). The major portion of the solution, however, flows from the pressure tank into the desorber *VII* which is essentially a two-tray froth apparatus. The first tray of the latter is used directly for desorption of gaseous ammonia from the solution, whereas the second tray performs the function of a heat exchanger (for cooling the gas), a water-vapour condenser, and a surge damper eliminating the sharp fluctuations in the gas concentration at the desorber outlet. An electric heater *X* is incorporated in the desorber to heat the solution on the first tray, and a cooling coil *VIII* is provided to cool the solution on the second tray. Both trays receive the solution from the overhead tank. As a result of water-vapour condensation, the excess solution flows from the second tray down onto the first one through a downcomer.

The design of the three-tray froth absorber, the system for controlling the liquid flows and changing their directions with respect to that of the gas-air mixture flow, the range of variations in the gas-air mixture flow rate, spraying density, and froth bed height (see Table 11), and the presence of a packed column permit the absorption process to be studied under a great variety of absorber operating conditions (see Table 12).

Table 11

Operating condition No.	Parameter	Designation	Dimension	Measurement range
1	Gas flow rate at the absorber inlet	G	m³/h	0-60
2	Liquid flow rate at the absorber inlet	L	l/h	0-50
3	NH₃ concentration in the gas-air mixture at the absorber inlet	C_{g_0}	vol. %	0-15
4	NH₃ concentration in the liquid at the absorber inlet	C_{l_0}	wt. %	0-4
5	Gas temperature	t_{g_i}	°C	10-50
6	Liquid temperature	t_{l_i}	°C	10-50
7	Pressure drop across the absorber tray	ΔP_i	mm H₂O	10-200
8	NH₃ concentration in the gas-air mixture at the absorber outlet	C_{g_i}	vol. %	0-10
9	NH₃ concentration in the liquid at the absorber outlet	C_{l_i}	wt. %	0-5
10	Froth bed height	H_i	mm	60-300
11	Froth bed cross-section	S	dm	1.0
12	Grid opening size	d	mm	3-6

The characteristics tabulated above are given for different liquid feed conditions determined by the solenoid valve positions. Operating conditions Nos. 14 and 15 are given for reference and are used only for the prestart check of transducer operation.

Changes in the hydrodynamic conditions in the reactor, occurring due to variations in the gas flow rate and froth bed height, permit analyzing the operation of the reactor on plug-flow, perfect-mixing, diffusion, cellular, and other models. The analysis involves definition of coefficients, their correction, testing of the models for adequacy, and determination of the effect of the above parameters on the mass-transfer coefficient k, efficiency η, and intensity I operation of the absorber.

II. STRUCTURAL FEATURES OF AUTOMATED ABSORPTION PLANTS

The following are the tasks to be accomplished in designing an automatic absorption plant control system: (a) selection and arrangement of local systems for automatic control of process variables; (b) construction of a system for automatic acquisition and reduction of process data using a computer; (c) selection and correction of models to ensure their adequacy to the real-time process; and (d) computer-aided search for optimal values of the process variables, which can be transmitted to local automatic control systems in the form of assignments, that is creation of an automatic process control system based on a control computer.

Table 12

Operat- ing condi- tion No.	Flow direction diagram	Num- ber of work- ing trays	Liquid is fed onto tray No.	Liquid flow from tray to tray	Mutual flows of gas and liquid	Valves in operation (on liquid lines) with reference to Fig. 63
1		3	3	3-2 2-1	counter	*7, 61, 18, 74, 17, 75, 73*
2		3	3 2	3-2 2-1	mixed	*7, 6, 61, 62, 18, 74, 73, 17, 75*
3		3	3 1	3-2 2-1	same	*7, 5, 63, 61, 18, 74, 17, 75, 73*
4		3	3 2 1	3-2 2-1	»	*5, 6, 7, 61, 62, 63, 18, 17, 73, 74, 75*
5		3	3 2	2-1	»	*6, 7, 18, 76, 17, 75, 73, 61, 62*
6		3	3 1	3-2	»	*5, 7, 63, 61, 18, 74, 17, 75, 73*
7		3	3 2 1	2-1	»	*5, 6, 7, 61, 62, 63, 18, 76, 17, 75, 73*

Continued

Operating condition No.	Flow direction diagram	Number of working trays	Liquid is fed onto tray No.	Liquid flow from tray to tray	Mutual flows of gas and liquid	Valves in operation (on liquid lines) with reference to Fig. 63
8		3	3 2 1	3-2	same	*5, 6, 7, 61, 63, 18, 74, 62, 17, 75, 73*
9		3	3 2 1	—	cross	*5, 6, 7, 63, 62, 73, 76, 77*
10		2	2	2-1	counter	*6, 62, 17, 75, 73*
11		2	2 1	2-1	mixed	*5, 6, 62, 63, 17, 75, 73*
12		2	2 1	—	cross	*5, 6, 17, 77, 73, 62, 63*
13*		1	1	—	same	*5, 63, 73*
14*		—	—	—	only gas **	—
15*		—	—	—	only liquid for analysis **	*3, 70, 71, 72, 76, 77*

* Feeding of the gas mixture into analyzers.
** Operating conditions Nos. 14 and 15 correspond to the prestart period.

The local systems of automatic process control, used in automation of absorption plants, comprise separate closed loops, each including four elements: transducer (measuring instrument), controller, actuator, and final control element. The controller operates in three modes— manual, transient, and automatic. In the manual mode, the position of the final control element of a pneumatic valve is changed from the
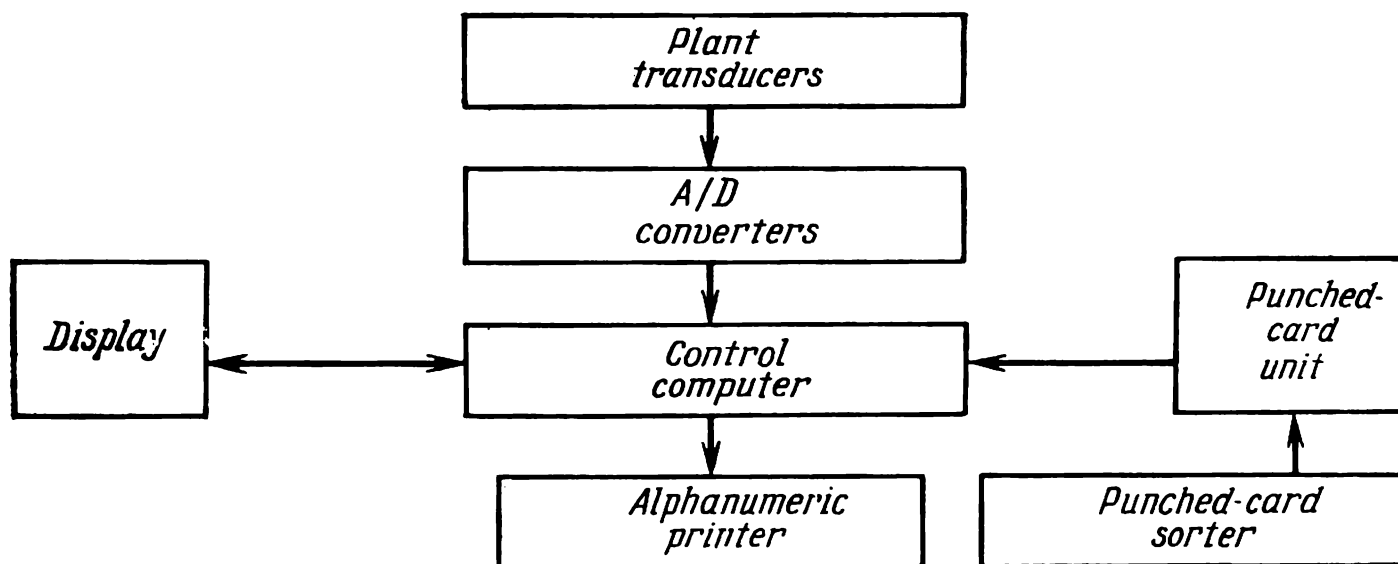
Fig. 64. Block diagram of the automatic data acquisition and reduction system

remote control panel of the controller, whereby the process variable is preset accordingly. In the automatic mode, the desired value of the process variable is preset in the controller, and the latter controls it automatically. In this case, the feedback signal corresponding to the process variable is applied from the transducer to the controller in which it is compared with the reference input. If the feedback signal differs from the reference input, according to the automation theory, the difference produces an actuating signal transmitted to the actuator (pneumatic control valves). Whether the value of the process variable should be changed manually or by a signal from the control computer the setting of the controller is done accordingly. In the case of absorber units, a unified system for automatic control of process variables has been established, that is a single type of automatic pneumatic controllers has been selected along with the same type of actuators — pneumatic valves. Only the transducers, or measuring instruments, are different. If a transducer sends information in the form of an electric signal, the latter is converted to a pneumatic signal with the aid of electropneumatic converters.

Automated absorption plants are also provided with a system of automatic acquisition and reduction of the data coming from the transducers, that is information on the status of process variables. This information is fundamental for solving all subsequent problems of process analysis and control.

The system operates as follows. The computer continuously monitors transducers in accordance with a given programme and processes the input data presenting them in tabular, graphic, or any other form convenient for analysis and subsequent processing of these data. The block diagram of the system is presented in Fig. 64. Thus, as soon as process data become available, one can proceed to their analysis or send an instruction from the display terminal to the computer for the latter to start processing the data.

III. BASIC EQUIPMENT OF AUTOMATED ABSORPTION PLANTS

Automated absorption plants form a constituent part of a whole complex comprising: (1) industrial absorbers; (2) instrumentation; (3) process data acquisition, recording and reduction facilities; (4) automatic process control facilities; (5) automatic protection and interlocking devices; (6) remote monitoring, control, protection, signalling and interlocking panels and boards; (7) a dynamic colour mimic diagram panel: (8) a digital control computer; and (9) peripheral process data recording and display devices.

The process scheme provides for joint as well as separate operation of the absorbers. This is done in order to increase the number of models used in the simulation of the absorption process and to enable comparison of the qualitative and quantitative performance parameters of different types of absorbers. The unit *VII* for desorption of ammonia from its aqueous solutions (see Fig. 63), common to both apparatus, is auxiliary and makes it possible to recover ammonia from its aqueous solutions and return it into the system. It also provides for continuous operation of the absorption plant in a closed-loop system, that is in the absorption-desorption mode with minimal losses of the starting chemicals. Since this unit is auxiliary, it is provided with local automation, but no provision is made for its automatic optimization and interfacing to the control computer.

The laboratory instrumentation includes industrial and laboratory types of instruments for measuring temperatures, flow rates, pressures, and other variables, as well as for quantitative and qualitative analysis of the reagents. They furnish all the necessary information concerning the process variables for analysing, optimizing and controlling the process.

The process data acquisition, recording and reduction facilities are intended for on-line monitoring and registration of the process variables.

The automatic control facilities ensure stabilization of some initial variables and implementation of control algorithms in the case of complex control actions, including those involving the use of the control computer.

The automatic protection and interlocking devices ensure operation of the absorption plant within specified limits of variable variation, generate alarm signals when significant deviations of process variables occur, and eliminate the disturbances that have caused these deviations.

The remote monitoring, control, protection, signalling and interlocking panels and boards allow operators to remotely control the process variables.

The control computer is intended for automatic acquisition and processing of the data from the process unit, simulation of the absorption process, automatic optimization and control of the process.

The above equipment of the laboratory permits performing the following operations: (1) manual remote control of the absorption plant, based on the readings of instruments of the control panel and the use of input variable stabilizers; (2) automatic control of the process, using local process variable controllers; (3) optimization of the process variables with the aid of an off-line computer; and (4) computer-aided optimization in a closed loop.

Such structure and equipment of the laboratory make it possible to organize the following cycle of laboratory works: (a) studying the kinetic features of a process and its hydrodynamic conditions; (b) process simulation and computer-aided analysis of the correction criteria used in the selection of a model as adequately representing the process as possible; (c) computer-aided analysis of optimization criteria for computing the optimal process conditions with the computer operating in off-line mode; and (d) computer-aided optimization and control of the process with the computer operating in a closed loop with the automated absorption plants.

IV. CONTENTS AND SEQUENCE OF LABORATORY WORKS

The experimental part includes a cycle of laboratory works involving both the froth absorber and the packed column:

1. Studying the chemical process of ammonia absorption by water.

2. Analysis of the absorption process models and correction criterion or selecting the most adequate model, with the aid of the computer and on-line data input.

3 Investigation of automatic process control systems and facilities.

4. Computer-aided analysis of correction and optimization criteria.

5. Optimized control of the absorption process with the computer operating in off-line mode.

6. Automatic optimization and control of the process in a closed loop with the control computer.

1. STUDYING AMMONIA ABSORPTION BY WATER IN AN AUTOMATED THREE-TRAY FROTH ABSORBER

The purpose of this work is to examine the effect of the basic input parameters of the process of ammonia absorption by water or aqueous ammonia solutions on the output variables and performance characteristics of the absorber unit.

In the case of absorption of gases, just as in most heterogeneous processes characterized by phase changes of substances, the determining kinetic equation is the following mass-transfer equation:

$$u = dG/d\tau = kF\Delta C, \qquad (3.10)$$

where $u = dG/d\tau$ is the process rate, that is the amount of a substance passing from one phase to another within unit time; k is the mass-transfer coefficient determining the process rate; F is the surface of contact between the reagents, determined by the hydrodynamic conditions of the process; and ΔC is the driving force of the process, given by the following expression for the absorption conditions:

$$\Delta C = C - C^*, \qquad (3.11)$$

in which C is the current actual component concentration in the donating phase, for example, gas phase during absorption, and C^* is the equilibrium concentration in the donating phase, for example, partial pressure of the absorbed component over the solution during absorption.

The quantities k and F determining the process rate are independent of the reagent concentrations, therefore, all other things being equal, they may remain invariable throughout the process.

In the case of heterogeneous processes, mass transfer and, respectively, changes in concentration are different and depend on the direction of material flows in the apparatus: cocurrent, countercurrent, or cross-current. The expressions for calculating the average driving force differ accordingly.

As far as absorption is concerned, one must also define efficiency as the ratio between the actually absorbed component and the equilibrium one, that is the degree of closeness to equilibrium,

$$\eta = (C_{g1} - C_{gf})/(C_{g1} - C_{\mathcal{E}}^*), \qquad (3.12)$$

where C_{g1} and C_{gf} stand for concentrations of the absorbed component in the gas at the inlet and outlet of the apparatus, respectively, and C_g^* is the equilibrium concentration.

Another important characteristic indicative of the efficiency of an apparatus is the intensity I of its operation, that is its capacity relative to a value representing the dimensions of the apparatus in question. Usually, in defining intensity, the capacity is related to

the apparatus volume v or its cross-sectional area S. The intensity I is defined, with respect to the gas (kg/(m³/h) or m³/(h/m³)), as

$$I = G\,(C_{gi} - C_{gf})/v; \qquad (3.13)$$

and, with respect to the liquid (kg/(m²/h) or m³/(h/m²)) as

$$I = L\,(C_{lf} - C_{li})/S, \qquad (3.13a)$$

where G and L are the flow rates of the gas and liquid phases, respectively; C_g and C_l are the concentrations of the absorbed component in the gas and liquid phases, respectively.
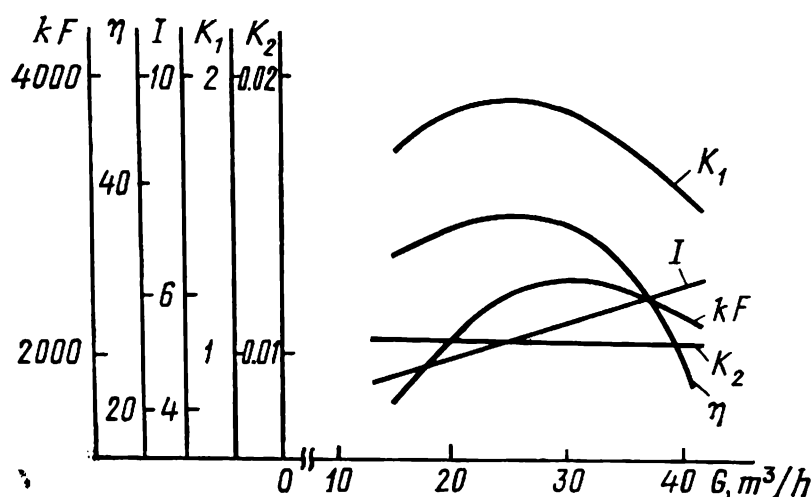
Fig. 65. Absorption process parameters versus gas-air mixture flow rate in froth apparatus

One of the basic requirements imposed on apparatus during their operation is maintaining optimal process conditions, that is conducting the process under conditions ensuring maximum yield of the end product at minimum production costs. In the case of absorption, the qualitative estimation of the optimality of the process conditions may involve the following process optimality criteria:

$$K_1 = I\eta, \qquad (3.14)$$

$$K_2 = I\eta/\Delta P, \qquad (3.15)$$

where K_1 and K_2 are the criteria taking into account the process efficiency η and its rate proportional to the reactor operation intensity I. The criterion K_2 also takes into account, indirectly, the power consumed to overcome the hydraulic resistance ΔP of the apparatus when the starting components are fed into the reaction zone. In the case of variations in the input parameters (gas flow rate G, liquid flow rate L, initial concentration C_i of the absorbed component in the gas phase at the absorber inlet, etc.), the values of K_1 and K_2 pass through maxima at points corresponding to the optimal values of these input variables (Fig. 65).

The assignment must specify the conditions leading to variations in a particular variable, its variation range, measurement ranges,

as well as the number of working trays and the pattern of gas and liquid flows with respect to each other.

After the assignment is known, students must define the control circuits, indicating the pneumatic valves, transducers, and automatic controllers plus the sequence in which individual units and apparatus are to be activated. Then, the system is activated, and the first of the specified process conditions is attained, that is the specified gas-air mixture and liquid flow rates and inlet concentrations, froth bed height, and other variables are set with the aid of controllers. As soon as the steady state is reached, the control computer is instructed from the display terminal to scan the transducers and compute the process variables. The monitoring and computation results are printed out by the control computer with the aid of an alphanumeric printer or shown on the display installed directly at the plant.

Example of Computation of Experimental Data. *Input variables*: $C_{g_1} = 3.287$; $G = 35.427$; $G_{l_1} = 0.061$; $L = 33.716$; $T_{1.in} = 16.858$; $T_{froth} = 21.599$; $T_{g.in} = 21.012$; $\Delta P_1 = 83.948$.

Output variables: $C_{g_2} = 1.89$; $C_{l_2} = 1.63$.

Computed values: efficiency $= 50.56$; $k = 6156.5$; $I = 13.29$; $K_1 = 6.7$; $K_2 = 0.8$; $\Delta C = 2.74$, where G is the gas-air mixture flow rate in the apparatus; L is the liquid flow rate on an absorber tray; C_{g_1} is the ammonia concentration in the gas at the absorber inlet; C_{g_2} is the ammonia concentration in the gas at the absorber outlet; C_{l_1} is the ammonia concentration in the liquid at the tray inlet; C_{l_2} is the ammonia concentration in the liquid at the tray outlet; $T_{1.in}$ is the liquid temperature at the tray inlet; T_{froth} is the froth bed temperature; $T_{g.in}$ is the gas temperature at the absorber inlet; and ΔP is the pressure drop across a tray.

After the transducers have been scanned and computations completed, one can proceed to the next set of operating conditions and so on to the last one. The results are tabulated as follows:

			Experimental data			
Ref. No.	G_1	G_{g_1}	C_{l_1}	L_1	C_{g_2}	t_{2in}
1	2	3	4	5	6	7

			Computed values			
ΔP_1	efficiency	k_M	K_1	K_2	I	ΔC
8	9	10	11	12	13	14

and curves are plotted showing η, I, k_M, K_1, and K_2 versus a particular variable (see Fig. 65). Finally, one must select the range of operating conditions in which the optimal ones will be found later.

Experimental Procedure. According to the assignment, the entire work is carried out in the laboratory under direct supervision and with participation of the instructor. Instruments, valves, the air blower, pumps, and other components of the system can be activated only by the instructor's permission. The instructor also permits changing over from one operating condition to another.

1. After the assignment has been given, determine the liquid flow pattern and the sequence of plant activation.

2. Preset the liquid flow pattern and the arrangement of instruments on the mimic panel.

3. Energize the absorber unit.

4. Switch on the mimic panel.

5. Energize the gas analyzers, refractometers, and secondary recorders.

6. Check the operation of the protection and interlocking circuitry.

7. Release the interlock of the pump.

8. Switch on the compressor.

9. Open the valve *25* (Fig. 63) after the pressure in the air line has reached 1.2 to 1.4 Pa.

10. Open the valves *23* and *24*, depending on the assignment.

11. Switch on the gas blower.

12. Adjust the air flow rate through the absorber with the aid of the pneumatic controller.

13. Open the valve on the ammonia bottle, then the pressure regulator *VI*.

14. Open the Hofer valve and feed the gas into the mixer.

15. Adjust the concentration in the gas-air mixture with the aid of the pneumatic controller.

16. Check whether the readings of all gas analyzers coincide.

17. Open the solenoid valves *70*, *71*, and *72* and check whether the readings of the refractometers coincide.

18. Close the solenoid valves *70*, *71*, and *72*.

19. Open the solenoid valves in accordance with the assignment.

20. Adjust the liquid flow rates on the absorber trays with the aid of the automatic controllers in accordance with the assignment.

21. Adjust the rate of the gas-air mixture feed into the desorber by means of the valve *23* so as to build up a froth bed in the desorber with the aid of the valve *78*, feed the ammonia liquor into the desorber from the overhead tank, and energize the heating coils.

22. Open the valve *87* and feed the ammonia liquor onto the second tray of the desorber.

23. Open the valve *85* and feed water into the cooler on the second tray of the desorber.

24. Complete the experiment under transient conditions with reference to the steady readings of the instruments. Read out the necessary values of the process variables and switch over to the next operating mode after the controller of the variable of interest has received an appropriate instruction. The variables may include the gas-air mixture flow rate G, liquid flow rate L on trays, gas concentration C_1 in the gas-air mixture at the absorber inlet, gas and liquid temperatures at the absorber inlet, and others.

25. After the experiment: (a) cut off the gas supply and close the ammonia bottle; (b) close the valves feeding the liquid onto the trays; (c) de-energize the heating coils of the desorber and cut off the liquid supply to both trays of the desorber; (d) switch off the gas blower; (e) de-energize the instruments; and (f) switch off the compressor.

2. COMPUTER SIMULATION OF AMMONIA ABSORPTION BY WATER IN A THREE-TRAY FROTH ABSORBER

The classification of mathematical models of reactors is based on the properties and states of concentration and temperature patterns in the reactor. The most complete models represent the transfer of a substance along and across the flow, rather than the variable physical properties of the reaction mixture. Thus, in studying the performance of reactors, a mathematical description (model) of the reactor is derived, that is a system of equations (differential or finite) that allow determining the changes in concentrations, temperature, and pressure. These equations are derived from the material, heat and momentum balances for the reactor as a whole or its infinitesimal elements.

Consider now some ideal mathematical models describing the process of mass transfer between the gas and liquid phases. The two-phase model of a plug-flow reactor with ideal displacement of the liquid and gas, both flowing in the same direction, is an idealized model according to which mixing of the phases in the direction of their flow is completely ruled out, while in a direction normal to the flow the concentration in individual phases is the same over the entire cross-sectional area.

To derive the equations, let us isolate a volume element dv in the reactor and develop a material balance equation for each phase. Then, the amount of the component coming in with the gas will be expressed as GC_{g_1}, G being the gas flow rate and C_{g_1} being the gas concentration at the absorber inlet. The amount of the component going out with the gas from the gas phase of the volume element

will be given by the expression

$$G\left(C_{g_1} + \frac{dC_g}{dH}\, dH\right).$$

The transition of the component from the gas phase of the volume element to the liquid phase through mass transfer will be expressed as

$$kF\,(C_g - C_g^*)\,SdH,$$

where k is the mass-transfer coefficient, F is the interfacial area, S is the cross-section of the volume element, and dH is its height.

Thus, the material balance equation for the gas phase takes the form

$$GC_{g_1} = G\left(C_g + \frac{dC_g}{dH}\, dH\right) + kF\,(C_g - C_g^*)\,SdH \qquad (3.16)$$

or, after transformation,

$$dC_g = -kF\,(C_g - C_g^*)\,d\,\frac{SH}{G}. \qquad (3.17)$$

Since $SH/G = \tau$, τ being the time spent by the components in the gas phase, then

$$dC_g/d\tau = -kF\,(C_g - C_g^*). \qquad (3.18)$$

The equation determining the component concentration in the liquid phase can be derived from the material balance of the entire reaction volume:

$$G\,(C_{g_1} - C_{g_2}) + L\,(C_{l_1} - C_{l_2}) = 0 \qquad (3.19)$$

hence,

$$C_{l_2} = \frac{G\,(C_{g_1} - C_{g_2}) + LC_{l_1}}{L}. \qquad (3.20)$$

Thus, for a model of ideal displacement of the liquid and gas flowing in a cocurrent (plug flow) we have the following system of equations:

$$\frac{dC_g}{d\tau} = -kF\,(C_g - C_g^*), \qquad (3.21)$$

$$C_{l_2} = \frac{G\,(C_{g_1} - C_{g_2}) + LC_{l_1}}{L},$$

where $C_g^* = f\,(C_l;\ T)$.

The boundary conditions are as follows:

at $\tau = 0$, $\quad C_g = C_{g_g}$, $\quad C_l = C_{l_1}$;

at $\tau = \max$, $\quad C_l = C_{l_2}$, $\quad C_g = C_{g_2}$.

In the case of countercurrent flow, the boundary conditions are different:

at $\tau = 0$, $\quad C_g = C_{g_1}$, $\quad C_l = C_{l_2}$;

at $\tau = \max$, $\quad C_g = C_{g_2}$, $\quad C_l = C_{l_1}$.

The two-phase model of perfect mixing of both the liquid and the gas is also an idealized model based on the assumption that the component concentration in the liquid and gas is the same throughout the volume.

The material balance equation for the entire volume can take the following general form:

Component in — Component out — Component loss as a result of mass transfer $= 0$.

The equation of material balance with respect to the gas phase is

$$G\left(C_{g_1} - C_{g_2}\right) - kF\left(C_{g_2} - C_g^*\right)v = 0, \qquad (3.22)$$

where C_{g_2} is the component concentration in the gas at the exit from the volume element.

The equation of material balance with respect to the liquid phase is

$$L\left(C_{l_1} - C_{l_2}\right) - kF\left(C_{l_2} - C_l^*\right)v = 0, \qquad (3.23)$$

in which C_{l_2} is the component concentration in the liquid at the exit from the volume element, L is the liquid flow rate in the volume element, and v is the reaction volume element.

Then, the material balance with respect to both the liquid and the gas will be

$$G\left(C_{g_1} - C_{g_2}\right) + L\left(C_{l_1} - C_{l_2}\right) = 0. \qquad (3.24)$$

Thus, we derive a system of two equations for the steady state:

$$\left.\begin{aligned} G\left(C_{g_1} - C_{g_2}\right) - kF\left(C_{g_2} - C_g^*\right)v = 0, \\ G\left(C_{g_1} - C_{g_2}\right) + L\left(C_{l_1} - C_{l_2}\right) = 0, \end{aligned}\right\} \qquad (3.25)$$

where $C_g^* = f\left(C_{l_2}; T\right)$.

Combinations of plug-flow and perfect-mixing models are possible, such as a two-phase model of ideal displacement of the gas and perfect mixing of the liquid. This idealized model is based on the assumption that the component concentration in the liquid is the same throughout the volume and equal to that at the exit from the volume, while the component concentration in the gas phase changes along the direction of gas flow as a result of mass transfer between the liquid and gas phases. There is no mixing in the gas phase in the direction of gas flow. The process as represented by this model is

given by the following system of equations:

$$C_{g2} = (C_{g1} - C_g^*)\, e^{-hF\tau} + C_g^*, \\ G\,(C_{g1} - C_{g2}) + L\,(C_{l_1} - C_{l_2}) = 0, \left.\right\} \qquad (3.26)$$

where $C_g^* = f\,(C_{l_2};\ T)$, τ being the time of residence of the components in the reaction volume.

The characteristics of many reactors are so close to the parameters of ideal models that real reactors may be regarded as almost ideal. For example, the above models adequately represent the process of absorption in froth apparatus at various gas flow rates. At high gas flow rates in laboratory apparatus, the perfect-mixing model is applicable to the liquid and gas phases. At lower gas flow rates, the turbulization of the system is less pronounced, and it is possible to use a model with perfect mixing of the liquid phase and ideal displacement of the gas phase. However, significant departures from the ideal are observed in some cases, caused by jet flows, circulation, or stagnation zones.

Fig. 66. Flow pattern in the phase contact zone in a plug-flow model with the gas breaking through and the liquid being completely mixed

The problems of non-ideal flow of liquids and gases are directly involved in transition from pilot to full-scale plants. When a process is studied on a pilot plant, a comprehensive analysis is made of the effect of various factors, including those associated with enlargement of apparatus, on the process parameters. If this effect is known precisely enough, the need to build a large pilot plant is eliminated. Consequently, in order to avoid serious errors in design, an appropriate correction for the departure of the flow from the ideal must be introduced. This departure is taken into account by using mathematical model correction factors which may include the circulation, break-through, turbulent diffusion and other coefficients.

Consider some non-ideal models used specifically in this work in conjunction with the froth apparatus or packed column.

Model 1. Plug-flow model with the gas breaking through and the liquid being perfectly mixed. Here, it is assumed that part of the gas does not participate in the mass transfer process, that is it moves in bubbles without any change in concentration in the zone of contact between the phases. In this case, the time of residence of the entire gas phase in the contact zone is the same, including that

part of the gas which takes part in mass transfer and the rest which
passes through the zone unchanged. The flow pattern in the phase
contact zone in such a model is illustrated in Fig. 66 and given by
the following system of equations:

$$\left.\begin{array}{l}
C_g = (C_{g1} - C_g^*)\, e^{-kF \frac{SH}{G}} + C_g^*, \\[2mm]
C_{l_2} = \dfrac{LC_{l_1} + G\,(C_{g1} - C_g)\,(1-n)}{L}, \\[2mm]
C_{g_2} = nC_{g1} + (1 + n)\, C_g,
\end{array}\right\} \qquad (3.27)$$

in which $C_g^* = f\,(C_{l_1};\ T)$ and n is the amount of break-through,
that is departure from the ideal.

Model 2. Plug-flow model with the gas breaking through and the
liquid undergoing ideal displacement; the phases flow in a cocurrent,
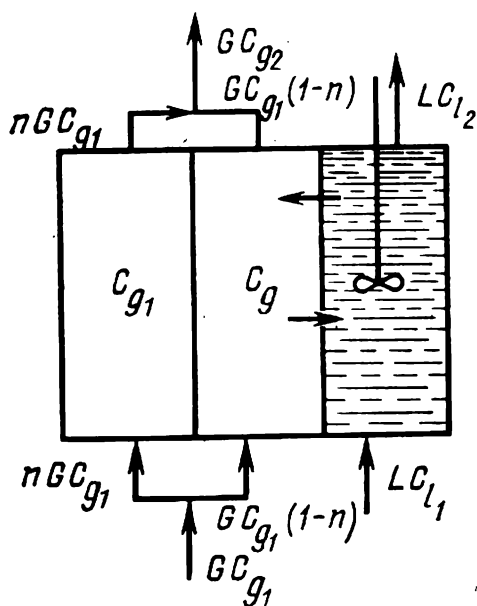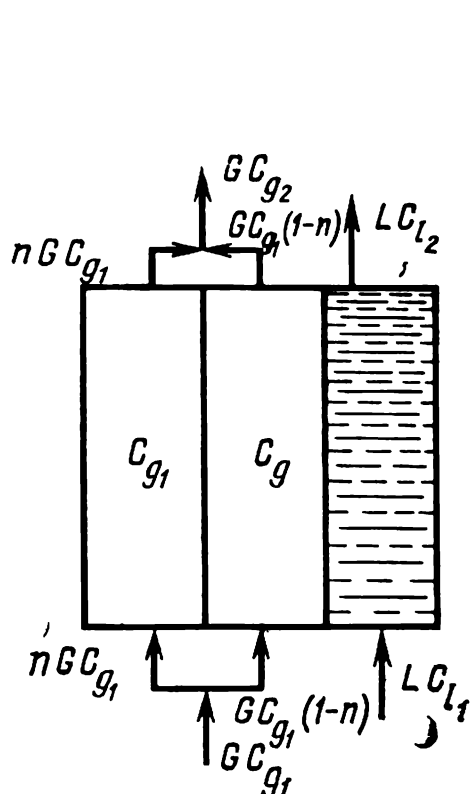

Fig. 67. Flow pattern in the
phase contact zone in a plug-
flow model with the gas break-
ing through and the liquid
undergoing ideal displacement
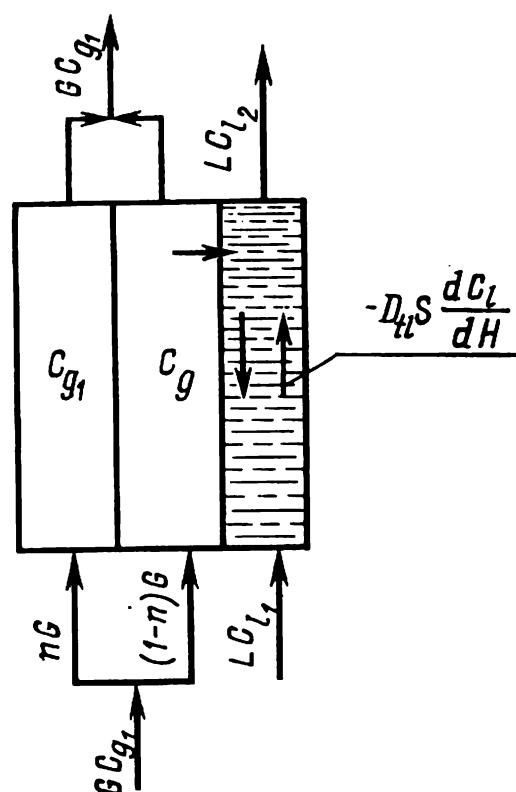
Fig. 68. Flow pattern in the
phase contact [zone in a plug-
flow model with the gas breaking
through and the liquid under-
going ideal displacement with
longitudinal diffusion

which is possible in a packed column. The flow pattern is shown in
Fig. 67. With such a flow pattern, part of the gas does not par-
ticipate in mass transfer. The latter occurs between part of the gas
phase and the liquid and is described as in the case of a model with
ideal displacement of both the gas and liquid phases flowing in
a cocurrent, the phase contact time being independent of the amount

of the gas involved in mass transfer. The mass transfer process in
an apparatus represented by such a model is given by the system of
equations

$$dC_g = -kF\frac{S}{G}(C_g - C_g^*)\,dH,$$

$$C_l = \frac{LC_{l_1} + G(C_{g_1} - C_g)(1-n)}{L},$$

$$C_g^* = f(C_l;\ T),$$

$$C_{g_2} = nC_{g_1} + (1-n)C_g,$$

$$\text{at }\ H = 0,\ C_g = C_{g_1},\ C_l = C_{l_1},$$
(3.28)

where n is the amount of break-through (departure from the ideal).
In the case of a countercurrent flow of the phases, we have a differ-
ent set of boundary conditions, namely,

$$\text{at }\ H = 0 \qquad C_g = C_{g_1}, \quad C_l = C_{l_2};$$
$$\text{at }\ H = H_{\max}, \quad C_g = C_{g_2}, \quad C_l = C_{l_1}.$$

Model 3. Plug-flow model with the gas breaking through and the
liquid undergoing ideal displacement with longitudinal diffusion.
Fig. 68, shows the flow pattern. In this case, part of the gas does not
take part in mass transfer, the time of residence of the gas phase
in the contact zone being the same for the whole phase. The liquid
flow pattern is intermediate between perfect mixing (at an infi-
nitely large diffusion coefficient) and plug flow (in the absence of diffu-
sion). In this model two correction factors are used (apart from kF):
n which is the amount of break-through and D_{tl} which is the coeffi-
cient of longitudinal diffusion in the liquid phase. The mass trans-
er process is described by the system of equations

$$dC_g = kF\frac{S}{G}(C_g - C_g^*)\,dH,$$

$$\frac{L}{S}\cdot\frac{dC_l}{dH} - D_{tl}\frac{d^2C_l}{dH^2} + kF(C_g - C_g^*) = 0,$$

$$C_g^* = f(C_l;\ T),$$

$$C_{g_2} = nC_{g_2} + (1-n)C_g,$$
(3.29)

$$\text{at }\ H = 0, \qquad C_g = C_{g_1}, \quad C_l = C_{l_1};$$
$$\text{at }\ H = H_{\max}, \quad C_g = C_{g_1}, \quad C_l = C_{l_2};$$ cocurrent

$$\text{at }\ H = 0, \qquad C_g = C_{g_1}, \quad C_l = C_{l_2};$$
$$\text{at }\ H = H_{\max}, \quad C_g = C_{g_2}, \quad C_l = C_{l_2}$$ countercurrent

Model 4. Model of cross-current flow of the phases with the liquid
phase being mixed in a direction normal to its flow with longitudinal
diffusion and the gas phase undergoing ideal displacement with

break-through. The pattern of flows is shown in Fig. 69. With such a flow pattern in the phase contact zone we use two correction factors in the mathematical model of the process (in addition to kF): n which is the amount of break-through in the gas phase and D_{tl} which is the coefficient of longitudinal diffusion in the liquid phase. Since with such a flow pattern the amount of break-through does not affect the phase contact time and in view of the fact that the component
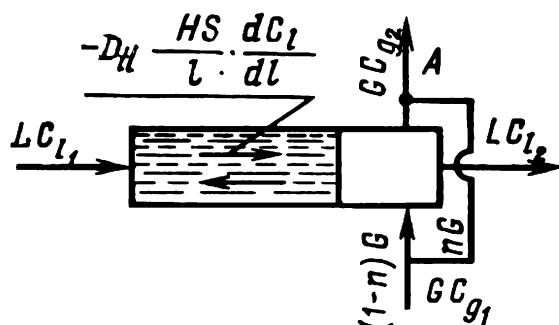
Fig. 69. Flow pattern in the phase contact zone in a model of cross-current flow of the phases with the liquid undergoing longitudinal diffusion and the gas undergoing ideal displacement with break-through

concentration in the gas phase is given by the equation of material balance at point A, we derive the following system of equations descriptive of the process of mass transfer in the apparatus at a given flow pattern:

$$
\left.
\begin{aligned}
& L\frac{dC_1}{dl} - D_{tl}\frac{HS}{l}\cdot\frac{d^2C_1}{dl^2} + \\
& + (C_{g_1} - (C_{g_1} - C^*)\, e^{-kF\frac{SH}{G}} + C^*)\,\frac{G\,(1-n)}{l} = 0, \\
& C^* = f\,(C_1;\ T), \\
& C = \frac{L\,(C_{l_1} - C_{l_2}) + (1-n)\,GC_{g_1}}{G\,(1-n)}, \\
& C_{g_2} = (1-n)\,C + nC_{g_1},
\end{aligned}
\right\}
$$

at $l = 0$, $C_1 = C_{1_1}$; at $l = l_{max}$, $C_1 = C_{1_2}$. (3.30)

Model 5. Model of countercurrent flow of the liquid and gas phases with longitudinal mixing (axial turbulent diffusion) in both. With the flow pattern of Fig. 70 we use two correction factors in the mathematical model of the process (in addition to k): D_{tg} which is the coefficient of turbulent diffusion in the gas phase and D_{tl} which is the coefficient of turbulent diffusion in the liquid phase The process of mass transfer in an apparatus having the above flow

pattern is described by the system of equations

$$\frac{G}{S} \cdot \frac{dC_g}{dH} - D_{tg} \frac{d^2 C_g}{dH^2} - kF\,(C_g - C_g^*) = 0,$$

$$\frac{L}{S} \cdot \frac{dC_l}{dH} - D_{tl} \frac{d^2 C_l}{dH^2} + kF\,(C_g - C_g^*) = 0, \qquad (3.31)$$

$$C_g^* = f\,(C_l;\ T),$$

at $H = 0$, $C_g = C_{g_1}$, $C_l = C_{l_2}$; at $H = H_{\max}$, $C_g = C_{g_2}$, $C_l = C_{l_1}$.

A prerequisite for using a mathematical model as a component of the system of optimization of a real-time process is the possibility of its revision in the course of operation of the plant. It is impossible to take into account, in a rigorous analytical manner, the effect of various hydrodynamic factors on the process with the desired accuracy. However, on the basis of the data received from the process unit during its operation (on-line data), one can refine the approximate mathematical model of the process.

Fig. 70. Flow pattern in the phase contact zone in a model of countercurrent flow of the liquid and gas phases with longitudinal mixing in both

Each one of the above-described models simulates a process under a definite set of conditions. Therefore, for given process conditions, one must select a model adequately representing the process. The selection procedure comprises so called parametric and structural synthesis of models. By structural synthesis is meant selection of a model representing the kinetics of the process and the hydrodynamics in the reactor, that is the pattern and direction of flows of the reacting substances with respect to one another. However, structural synthesis permits defining only the qualitative aspect of the process.

To define the quantitative aspect of a process parametric synthesis of models is used, that is quantitative definition of kinetic coefficients and flow rates in the course of a reaction. The structural and parametric syntheses of models are based on the experimental data obtained within a given range of variations in the process variables.

One of the tasks of this work is to define, with the aid of a computer, a model adequately representing a process within a particular range of variations in the process conditions in an absorption plant. To this end, a set of four models 1 through 4 is made up, each model providing an approximate description of the absorption process with due account for its conditions. On the basis of this set of models and the data concerning the status of process variables within the

specified variation range, the control computer performs parametric synthesis of each model, that is finds the minimum of the correction criterion.

Taken as the correction criterion in the synthesis of a mathematical model of the process may be the convergence of experimental and computed output variables or the convergence of the experimental and computed process efficiency parameters (η, K_1, K_2, I). The correction criterion is computed as follows:

$$Z_c = \sum_{j=1}^{j=N} \sum_{i=1}^{i=M} A_i \left(C_{\text{out. comp. } ijk} - C_{\text{out. exp. } ijk} \right)^2 \qquad (3.32)$$

or

$$Z_c = \sum_{j=1}^{j=N} \sum_{i=1}^{i=M} A_i \left(P_{\text{comp. } ijk} - P_{\text{exp. } ijk} \right)^2, \qquad (3.33)$$

in which Z_c is the correction criterion of a model; i is the number of the output variable or process efficiency parameter; j is the number of operating modes; k is the model number; A is the mass parameter; $C_{\text{out. comp}}$ is the computed output variable; $C_{\text{out. exp}}$ is the experimental output variable; $P_{\text{comp.}}$ is the computed efficiency parameter; $P_{\text{exp.}}$ is the experimental efficiency parameter; M is the number of output variables or process efficiency parameters; and N is the number of operating modes within a given range of variations in the process variables.

The model can be refined through selection or computation of some coefficients of the model, the physical meaning of which need not be stipulated. The coefficients to be corrected may include physical constants that cannot be precisely defined or measured at the plant (e.g., interfacial area, mass-transfer coefficient, heat-transfer coefficient, etc.). Each one of the models that provide an approximate description of the process must be subjected to parametric synthesis, that is the correction factors must be selected such that the correction criterion is minimal for each model. This is to be followed by structural synthesis, that is selection of a model having the minimal correction criterion within a given range of variations in the process variables.

Activation of the plant and changeover from one operating mode to another remain similar to Work 1 (p. 235). Thus, after the first set of conditions from the chosen range has been established and stabilized, the control computer is instructed from the display terminal to scan the transducers, after which the next operating mode is initiated, then the next and so on till the entire chosen range is covered. The process data acquired as a result of monitoring of the transducers are stored in the control computer. Finally, the control computer is instructed to perform parametric synthesis

for each model:

$$Z_1 = f^1 (kF_1; \ n_1), \tag{3.34}$$

$$Z_2 = f_2 (kF_2; \ n_2), \tag{3.35}$$

$$Z_3 = f_3 (kF_3; \ n_3; \ D_{tl_s}), \tag{3.36}$$

$$Z_4 = f_4 (kF_4; \ n_4; \ D_{tl_s}), \tag{3.37}$$

where kF_c, n_c, and D_{tl_c} are correction factors.

The block diagram of parametric synthesis is given in Fig. 71. Blocks I through V are implemented in the control computer. *Block* I
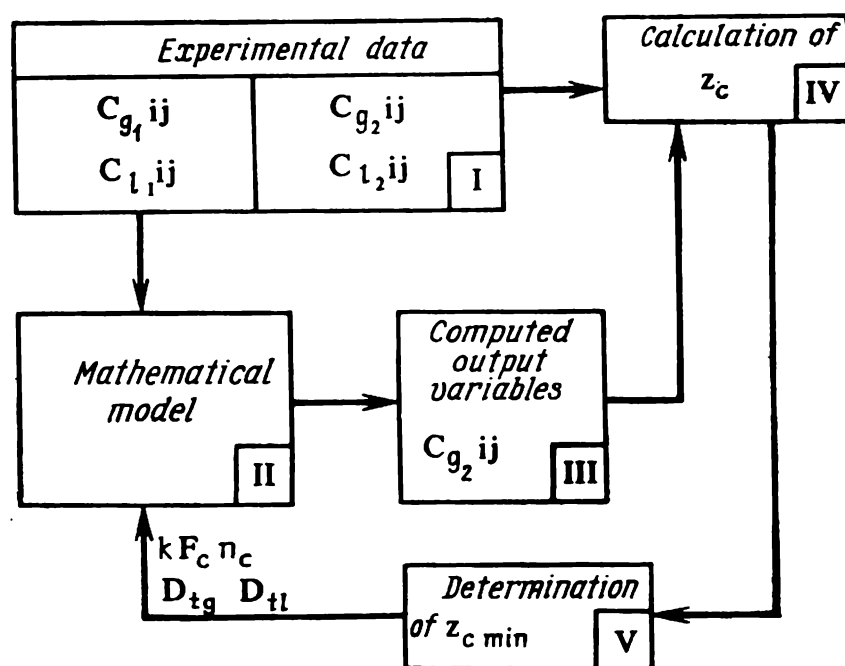
Fig. 71. Block diagram of parametric synthesis

is intended for storage of experimental data, that is values of input and output variables of the plant under all operating conditions. *Block* II is the mathematical model of the process, in which the output variables of the process are computed at current values of kF_c, n_c, and D_{tl_c}. *Block* III is intended for storage of the output process variables computed on the basis of models for all operating conditions. *Block* IV is intended for computation of the model adequacy criterion Z_e. *Block* V is intended to define the correction factors kF_c, n_c, and D_{tl_c}.

The reduced experimental data (determination of H, L, and C_{li}) corresponding to all operating conditions are fed into block I. Then, following an instruction from the terminal, the output process variables are computed in block II for all operating conditions at the first approximate values of the model correction factors kF_c, n_c, and D_{tl_c}. The computed output variables are stored in block III.

After the model-based computation for all operating conditions has been completed, the adequacy criteria Z_c are computed in block IV from Eqs. (3.32) and (3.33). The cycle is then repeated for definition and comparison of each preceding value of Z_c with the subsequent one. After that, the minimum of the function is found, that is new approximate values of kF_c, n_c, and D_{tl} are defined in block V by the algorithm of searching for the extremum of the function $Z_c = f (kF_c, n_c, D_{tl_c})$ and transmitted to block II. In the latter, new values of the output process variables are computed to be sent to block III, then to block IV. The new value of Z_c is compared with the preceding one in block V, and new approximate values of kF_c, n_c, and D_{tl_c} are generated. The search for kF_c, n_c, and D_{tlc} results in a minimum of the function for a given model. In this case, entered in storage are the values of kF_c, n_c, D_{tl_c}, and Z_c as well as the output variables computed on the model basis at the derived values of kF_c, n_c, and D_{tlc} (Z_c = min).

Thus ends the parametric synthesis of the first model, and the software of the control computer initiates parametric synthesis of the next model. After the parametric synthesis of all models has been completed, the computation results are printed out and displayed as follows: Model...

$$Z_c, \; kF_c, \; D_{tlc}, \; n_c.$$

Input variables: C_{g_1}, C_{l_1}, L, G, t, ΔP_1, ΔP_2, ΔP_3. Experimental output variables: C_{g_2}, C_{l_2}, η, I, K_1, K_2. Computed output variables: C_{g_2}, C_{l_2}, η, I, K_1, K_2.

3. OPTIMIZATION OF THE PROCESS OF AMMONIA ABSORPTION BY WATER IN A THREE-TRAY FROTH ABSORBER WITH THE CONTROL COMPUTER OPERATING IN OFF-LINE MODE

To optimize a process one must first of all select an optimization criterion. For specific conditions a process or cost criterion is selected, on the basis of which the efficiency function is generated, which represents the dependence of the optimization criterion on the variables affecting its value, that is a formula for its computation is derived.

To define the optimal process conditions, equations describing the process (selected mathematical model of the process) are solved together with the equation in which the optimality criterion is related to process variables. The definition of optimal conditions boils down to search for such input process variables at which the optimality criterion has an extremal value.

Since the cost efficiency analysis of the laboratory absorption plant is somewhat arbitrary, process criteria are used in this work

as the optimization criteria, which permit meeting some special requirements: (a) criterion K_1—absorber operation intensity times its efficiency (3.14); (b) criterion K_2—ratio of criterion K_1 to hydraulic resistance loss ΔP on the absorber trays (3.15).
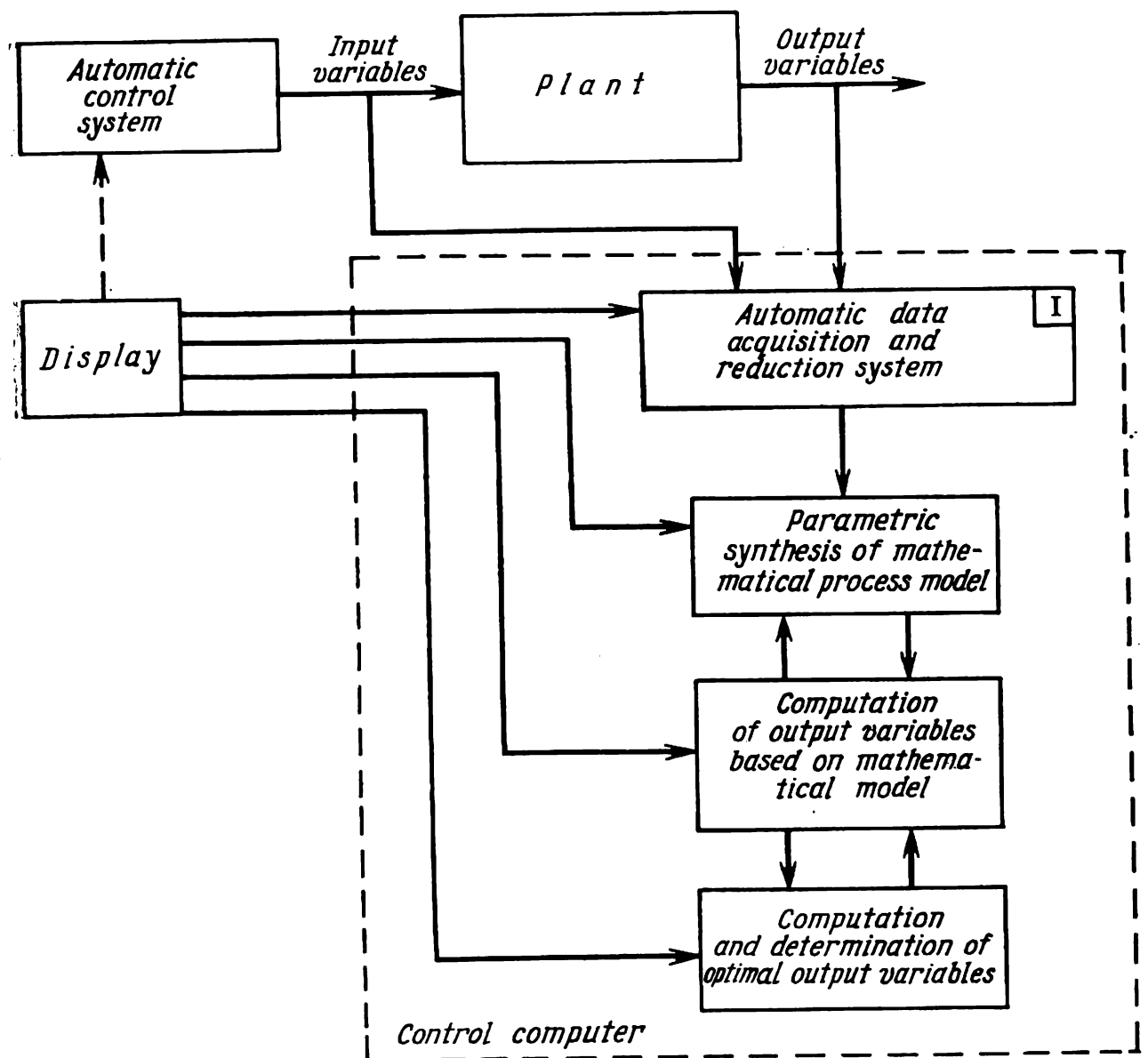
Fig. 72. Block diagram f the algorithm of optimal absorption process control

The sequence of plant activation and changeover from one operating mode to another as well as de-activation of the unit remains the same as in the preceding works.

The procedure of interaction with the computer resides in that an instruction is sent from the display terminal for the computer to compute optimal input process variables using the selected mathematical model and the specified optimality criterion K_1 or K_2, (3.14) or (3.15) (see Part 2 of this work). The block diagram of the absorption process optimization algorithm is shown in Fig. 72.

The control computer computes the input variables and presents them on the screen of the display installed at the plant. The computed input variables are transmitted to the plant. After the process steadies itself, another instruction must be sent for the computer to monitor the transducers and start data reduction since the correction factors must be constantly refined during optimization, with the range of variations in input variables being narrowed and the latter being brought closer to the optimal values. Therefore, after the data reduction is over, the computer is instructed to proceed to parametric synthesis of the selected model and computation of the optimal absorption process conditions with refined model correction factors. Thus, each time a set of optimal conditions has been computed, it must be implemented in the plant, then fresh data are received from the latter for the model to be refined (to be subjected to parametric synthesis), and the refined model is used in the computation of a new set of optimal conditions, which will come still closer to the absolute optimum. The more accurate the selection of the mathematical model, the less is the number of steps to be taken in achieving the equality of the process optimality criteria computed on the basis of the model and process data.

The results for each step are displayed or printed out in the following form:

Step I...
Model...
Computed parameters: C_{g_1}, C_{l_1}, G, L, ΔP_1, ΔP_2, ΔP_3, C_{g_2}, C_{l_2}, k.
Experimental parameters: C_{g_1}, C_{l_1}, k.
Step II...
Model..., etc.

4. STUDYING THE PROCESS OF AMMONIA ABSORPTION BY WATER IN THE PACKED COLUMN

The experimental work also involves studying the output variables and parameters of ammonia absorption by water in the packed column with a view to defining the optimal range of values of the input and output variables as well as other process parameters. The input variables of the process include the rate of liquid feed into the column, the gas-air mixture flow rate G, and the ammonia concentrations in the gas-air mixture (C_{g_1}) and in the liquid (C_{l_1}). The output variables and other parameters include ammonia concentrations in the gas-air mixture (C_{g_2}) and in the liquid (C_{l_2}) between the column sections, efficiency η of the apparatus, its operation intensity I, criteria K_1 (3.37) and K_2 (3.38), pressure drops across each column section $(\Delta P_1$, ΔP_2, $\Delta P_3)$ and across the entire column $(\Delta P = \Delta P_1 + \Delta P_2 + \Delta P_3)$. The experiment is based on

the instrumentation and automatic control facilities at the plant plus the control computer.

After the assignment has become known, students establish the sequence of initiating the flows through the plant, indicating all the valves involved and the order of their actuation. Then, the plant is activated, and the packed column is brought to the first operating mode. After stabilization of the latter, the computer is instructed from the display terminal to scan the transducers and compute the process variables and parameters. The results are displayed.

The displayed data are used to fill tables and to plot curves showing the output variables and process parameters versus an input variable, appropriate conclusions being drawn as to the position of the optimal operating conditions range, from the criteria K_1 and K_2, and the effect of the input variable on the process parameters and output variables.

The first step of the experimental procedure is to define the liquid and gas flow pattern in the plant. Then, the plant is energized, and the mimic panel is switched on. Also energized are the gas analyzers, refractometers, and secondary recorders. The operation of the alarm and protection system is checked. The interlock of the pump is released. The compressor is switched on. After a pressure of 1.2 to 1.4 MPa has been attained in the air lines (see Fig. 63), the valves *20*, *23*, and *25* are opened. Next, the gas blower is activated. The air flow rate in the absorber is adjusted by means of a pneumatic controller. The valve on the ammonia bottle then the pressure regulator *VI* are opened. Also opened is the Hofer valve to feed air into the mixer. The ammonia concentration in the gas-air mixture is adjusted with the aid of a pneumatic controller. Another pneumatic controller is used to adjust the liquid flow rate in the column. The feed rate of the gas-air mixture into the desorber is adjusted by the valve *23* so as to build up a froth bed in the latter and to feed into it ammonia liquor from the overhead tank (by opening the valve *78*), after which the heating coils are energized. The valve *87* is opened to feed the ammonia liquor onto the second tray of the desorber. Then, the valve *85* is opened to deliver water into the cooler on the second tray of the desorber. After the system has come out of the transient state, which is indicated by the stabilized instrument readings, the specified variables are read out (following an instruction from the display terminal to the control computer), and switchover to the next operating mode takes place. The variables may include the gas-air mixture flow rate in the absorber, ammonia concentration in the gas-air mixture, temperature, liquid flow rate in the absorber, liquid concentration, and others. Then, the dependence of the output variables (C_{g_2}, C_{l_2}, etc.) and computed parameters (kF, η, I, K_1, K_2) on the input variables (G, L, C_{g_1}, C_{l_1},

etc.) is studied with the aid of the automatic data acquisition and reduction system. The results of this stage of the experiment are tabulated and graphically represented.

After the experiment: (a) cut off the gas supply by closing the ammonia bottle; (b) cut off the water supply into the absorber; (c) de-energize the heating coils and stop feeding the liquid into the desorber; (d) switch off the gas blower; and (e) switch off the compressor.

5. SIMULATION OF AMMONIA ABSORPTION BY WATER IN THE PACKED COLUMN

At this juncture, students must select a mathematical model descriptive of the process of absorption in the packed column within a given range of variations in input variables. The laboratory work involves structural and parametric syntheses of the model. The structural synthesis is aimed at defining a model most adequate to the process in the packed column, on the basis of a set of models (see Part 2 of this work).

The most suitable is model 2—ideal displacement of the gas phase with break-through and ideal displacement of the liquid in a countercurrent flow, or model 5—countercurrent flow with longitudinal mixing (turbulent diffusion) in both phases. Each model is subjected to parametric synthesis based on the process data, that is the amount of break-through n and the values of kF for model 2 and the coefficients of turbulent diffusion in the gas and liquid phases (D_{tg} and D_{tl}) and the values of kF for model 5 are determined. Taken as the adequacy criterion is the quantity

$$Z_c = |C_{1exp} - C_{1comp}| + |B_{1exp} - B_{1comp}| +$$

$$+ |C_{2exp} - C_{2comp}| + |C_{2l.\,exp} - C_{2l.\,comp}| +$$

$$+ |C_{3g.\,exp} - C_{3g.\,comp}| + |C_{3l.\,exp} - C_{3l.\,comp}|. \qquad (3.38)$$

Z_c is defined for both models, for each set of steady operating conditions in the packed column, and the model with the lowest value of Z_c is taken. The control computer will run data acquisition and reduction programmes, the programme of computation of the process on the basis of models 2 and 5, and the programme of parametric synthesis of mathematical models.

The sequence of activation and de-activation of the plant is the same as in Part 4 of this work.

After activation, the plant is made to operate in the first of the selected modes. The computer is then instructed to scan the transducers, start data reduction, and proceed to parametric synthesis of models 2 and 5. After the parametric synthesis of both models is over, the next operating mode is initiated. Shown on the display

screen are the model correction factors, correction criteria, as well as the values of the computed and experimental output variables and performance parameters of the packed column. For example, input variables: C_{g_1}, C_{l_1}, L, G, t, ΔP_1, ΔP_2, ΔP_3; output variables: C_{g_2}, C_{l_2}, η, I, K_1, K_2.
Model...

$$Z_c, \ kF, \ n, \ D_{tg}, \ D_{tl}.$$

Output variables: C_{g_2}, C_{l_2}, n, I, K_1, K_2.
After the data of the last operating mode have been reduced, the plant is de-activated. After the experiment, analysis is made of the values of the adequacy criteria, output variables, and other parameters of the packed column operation, computed on the basis of the models, and a conclusion is drawn as to which process model to select, that is structural synthesis is performed.

6. OPTIMIZATION OF THE PROCESS IN THE PACKED COLUMN

Another task to be accomplished in this work is optimization of the absorption process in the packed column, using an appropriate mathematical model. The optimization involves solution of the equations descriptive of the process as well as the equation in which the optimality criterion is related to the process variables.

The plant is activated and de-activated and the switchover from one operating mode to another is carried out in the same sequence as described in Part 4 of this work.

The computer is instructed to compute the optimal process conditions on the basis of the model selected as described in Part 5 of this work. The computed process conditions are sent from the control computer to the display of the plant. The computed variables are set at the plant with the aid of automatic controllers and, after the operating mode has stabilized, the control computer is instructed to start data acquisition and reduction, parametric synthesis, and computation of the optimal conditions, that is the next step in the search for optimal process conditions is embarked upon.

The computations (search) are over when the optimality criteria, computed from the experimental and computed data, become equal. The results of each step are displayed in the following form:
Step 1...
Model...

$$Z_c, \ kF, \ n, \ D_{tg}, \ D_{tl}.$$

Computed parameters: C_{g_1}, C_{l_1}, G, L, ΔP_1, ΔP_2, ΔP_3, C_{g_2}, C_{l_2}, k.
Experimental (output) parameters: C_{g_2}, C_{l_2}.

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Instructions to the Laboratory Work "Automated Absorption Plants"

The absorption plants are to be assembled in compliance with the requirements imposed on similar plants in the chemical industry.

The automatic protection and interlocking systems and facilities rule out short circuits and fire and permit eliminating the causes of accidents at the plants. Hazards to the health of the personnel and those standing near the plants may arise as a result of sudden loss of sealing of the gas and liquid lines.

As soon as ammonia odour appears in the laboratory, cut off the supply of the gas into the working line, switch off all instruments, find out what caused the leakage, and stop it.

Leakage of ammonia may cause intoxication because it irritates the upper respiratory tract. High concentrations bring about sharp pain in the eyes and lacrimation, signs of asphyxia, intense coughing spells, dizziness, pains in the stomach, and nausea. The first aid in the case of ammonia intoxication consists in taking the affected person out to breathe some fresh air and, if the intoxication is severe, resorting to artificial respiration. If necessary, call a doctor.

Students are allowed to work at the plant only in the presence of the instructor and after they have been instructed in safety precautions.

The working station must be provided with (a) filtering protective gas masks of the КД, ВК or M type; (b) a carbon-dioxide fire extinguisher of the ОУ-5 type; and (c) dielectric rubber gloves.

LABORATORY WORK 22. PERFORMANCE ANALYSIS OF LIQUID-PHASE REACTORS

The automated plant is intended for performance analysis of homogeneous liquid-phase perfectly mixed reactors operating intermittently, semicontinuously, continuously, and in a series cascade, as well as a tubular continuously operating plug-flow reactor.

The comprehensive laboratory works are based on the following logical sequence: studying the kinetics of the chemical reaction, design and analysis of the reactors, simulation, and automation of the process with computer-aided optimization.

This work is based on the homogeneous chemical reaction of saponification of an ester with alkalis, proceeding according to the equation

$$CH_3COOC_2H_5 + OH^- \rightleftharpoons CH_3COO^- + C_2H_5OH$$
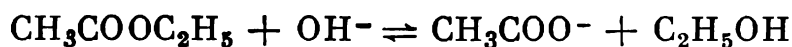
The reactions of ester saponification with sodium hydroxide in dilute solutions at equimolecular reagent ratios are of the second

order. The rate of the irreversible reaction is given by

$$-dC_A/d\tau = kC_AC_B, \tag{3.39}$$

in which C_A and C_B are current concentrations of the starting reagents A and B, k is the reaction rate constant, and τ is time.

After integration of Eq. (3.39) we have

$$k = \frac{1}{\tau(C_{A_0}-C_{B_0})} \ln \frac{C_{B_0}(C_{A_0}-C_x)}{C_{A_0}(C_{B_0}-C_x)}. \tag{3.40}$$

If $C_A = C_B$, Eq. (3.39) takes the form

$$-dC_A/d\tau = kC_A^2, \tag{3.41}$$

whose integration gives

$$k = \frac{C_x}{\tau C_{A_0}(C_{A_0}-C_x)}, \tag{3.42}$$

at $C_A = C_{A_0}/2$,

$$k = 1/\tau_{1/2}C_{A_0}; \quad \tau_{1/2} = 1/kC_{A_0}. \tag{3.43}$$

The reagents being in stoichiometric ratios, the reaction order can be determined from the data of a single kinetic experiment. To determine the order of the reaction use is often made of the method of selection of the kinetic equation and the graphic method. The latter consists in the following: time τ is plotted on the abscissa, while plotted on the ordinate are $\log C$, $1/C$, and $1/C^2$ for the reaction under investigation. Three lines are produced as a result; the line corresponding to the order of this reaction will be straight. Given below are the differential equations of the rates of reactions of different orders and their solutions (Table 13).

Table 13

Reaction order	Reaction rate equation	Solution of the equation
1	$-dC/d\tau = k_1C$	$\log C = a_1 - k_1$
2	$-dC/d\tau = k_2C^2$	$\dfrac{1}{C} = a_2 - k_2$
3	$-dC/d\tau = k_2C^3$	$\dfrac{1}{C^2} = a_3 - 2k_3$

The temperature dependence of the reaction rate constant is given by the Arrhenius equation whose logarithmic form can be written as

$$\ln k = \ln k_0 - E/RT, \tag{3.44}$$

where k is the reaction rate constant, k_0 is the temperature-independent factor, E is the activation energy, R is the universal gas constant, and T is absolute temperature. As can be inferred from Eq. (3.44), the relation between the logarithm of the rate constant and inverse temperature is linear.

The component concentration in the reaction mixture is determined in this work by way of physicochemical analysis based on variations in the conductance of the reaction mixture in the course of the reaction. To carry out this analysis one must know the constant of the vessel used for measurement. The resistance of the electrolyte solution depends on concentration, electrode area, electrode spacing, shape and mutual arrangement of the electrodes, and solution volume in the vessel. The overall resistance of the vessel with the solution is found from the equation

$$R = \beta \rho L/s, \tag{3.45}$$

where β is a coefficient which is a function of the vessel geometry, L is the distance between the electrodes, s is the electrode area, and ρ is the solution resistivity.

If β, L, and s remain constant throughout the measurement, the conductivity will be

$$\varkappa = 1/\rho = n/R, \tag{3.46}$$

where R is the solution resistance.

The coefficient $n = \beta L/s$ is referred to as the vessel constant in conductivity measurements.

Eq. (3.46) is used to calculate the conductivity $\varkappa_0$ of the initial sodium hydroxide solution at the solution resistance R_0.

The concentration of the sodium hydroxide solution is defined as

$$C_{\text{alk}}^0 = \frac{1000 \varkappa_0}{197 \left[1 + 0.019 \left(t - 18\right)\right]} \,. \tag{3.47}$$

Usually, a 0.02 N solution of NaOH is used. The concentration of ethanol or sodium acetate, equal to that of the sodium hydroxide (or ethyl acetate) entering into the reaction, is determined from the equation

$$C_x = \frac{1000 \left(\varkappa_0 - \varkappa_\tau\right)}{139 \left[1 + 0.0165 \left(t - 18\right)\right]} \,, \tag{3.48}$$

where $\varkappa_\tau$ is the conductivity at a given point in time.

The initial ethyl acetate concentration C_{ea} is calculated using Eq. (3.48) in which $\varkappa_\tau$ is substituted by $\varkappa_\infty$ which is the conductivity at the end of the reaction.

The obtained values of C_{alk}^0, C_{ea}^0, and C_x are substituted into Eq. (3.40), and the reaction rate constant is determined. If the alkali is taken in a different concentration, the denominator of Eqs. (3.47) and (3.48) is changed.

Series Cascade of Perfectly Mixed Reactors. A cascade of perfectly mixed reactors is the principal subject of laboratory studies. In view of the incompleteness of the process in a single-stage perfectly mixed reactor, use is made of reactors arranged in series, or a cascade of perfectly mixed reactors. The greater the number of reactors in a cascade, the more closely the system approaches plug-flow conditions. Several methods can be recommended for calculating the number of cascade stages.

The *algebraic method* permits determining the reagent concentration at the outlet of any reactor in the cascade plus the number of series-connected reactors, for which purpose the following equations are used:

$$C_{Am} = C_{A_0}/(1 + k\tau)^m, \tag{3.49}$$

$$m = \log \frac{C_{A_0}}{C_{Am}} \Big/ \log (1 + k\tau), \tag{3.50}$$

in which m is the number of reactors in the cascade; C_{A_0} and C_A stand for the initial and final concentrations of the reagent A, respectively; k is the reaction rate constant; and τ is the residence time.

Eqs. (3.49) and (3.50) hold if the reaction volumes and isothermal conditions in the reactors are equivalent. The application of the algebraic method to high-order reactions involves difficulties.

The *graphic method* of calculating a cascade of reactors is more convenient in most cases than the algebraic one and is based on transformation of the characteristic equation

$$\tau = (C_{A_0} - C_A)/u_A \tag{3.51}$$

to the form

$$u_{Am} = -\frac{C_{Am}}{\tau} + \frac{C_{Am-1}}{\tau} = -\frac{1}{\tau} C_{Am} + \frac{C_{Am-1}}{\tau}. \tag{3.52}$$

Eq. (3.52) is an equation of the straight line representing the relationship between the concentration C_A at the outlet of the mth reactor of the cascade and the rate u_{Am} of the reaction in that reactor. The slope of this line is $-1/\tau$, the line intersecting the x axis at the point C_A (Fig. 73).

To determine the concentrations at any stage, a straight line is drawn from the point C_{A_0} at an angle α, till it intersects the $u = = f\,(C)$ curve, and the perpendicular dropped from the point of intersection gives the values of the concentration at the outlet of each stage of the cascade and at the inlet of the subsequent one, and so on. If the reactor volumes are equal, the reagent residence time is the same; consequently, the straight lines will be parallel, and the construction continues till the predetermined concentration is reached. The obtained number of points will correspond to the necessary number of reactors.

Plug-Flow Model for a Tubular Reactor. The equation for the plug-flow model under steady-state (stationary) conditions takes the form

$$w \, (\partial C_A / \partial H) = -u_A, \tag{3.53}$$

where w is the linear flow rate; $w \, (\partial C_A / \partial H)$ is the difference between the amounts of the substance A, entering an infinitesimal element of the reactor and exiting from it (convective transfer) per unit
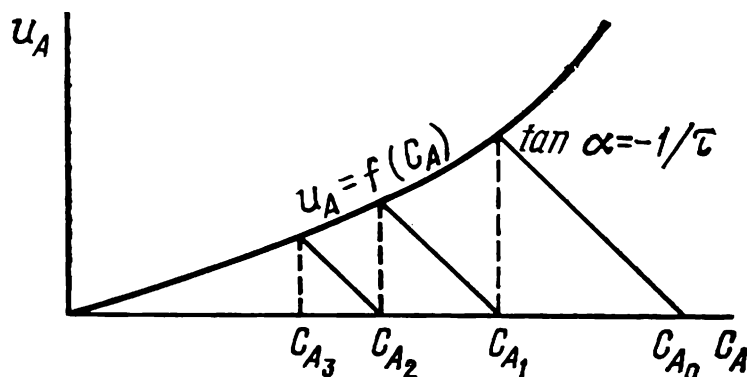
Fig. 73. Calculation of a perfectly mixed reactor cascade

time; H is the reactor length; and u_A is the rate of consumption of the substance A in the course of the reaction.

If the reaction proceeds without any change in volume, the percentage conversion $x_H = (C_{A_0} - C_A)/C_{A_0}$, and the kinetic equation for an nth-order irreversible reaction, with respect to the main component $(-u) = kC_A{}^n$, takes the form

$$\tau = \frac{1}{k} \, C_{A_0}^{1-n} \int\limits_0^{x_A} \frac{dx}{(1 - x_A)^n}. \tag{3.54}$$

After integration, for $n = 1$

$$\tau = - \frac{\ln (1 - x_H)}{k}. \tag{3.55}$$

For $n \neq 1$

$$\tau = \frac{C_{A_0}^{1-n}}{(n-1) \, k} \, [(1 - x_H)^{1-n} - 1], \tag{3.56}$$

in which τ is the residence time in the plug-flow reactor.

Description of the Automated Plant and Experimental Procedure

The automated plant is a complex including the process reactor, automatic control and computer facilities. With the aid of the automatic control facilities, operator's panel, and alphanumeric printer,

Fig. 74. Automated plant used in performance analysis of liquid-phase reactors

Reaction mass line
Ethyl acetate line
Alkali line
CO_2 protection line
Cold water line
Hot water line
Treated water line
Sewer line

forming part of the control computer, one can perform laboratory works at the plant, similar to those described in Work 21. The instrumentation and automatic control facilities are intended, primarily, for adjustment of such process variables as temperature, flow rate, level, concentration, and pH. They are also used to remotely start the plant, bring it to the specified operating conditions, stabilize the above-listed parameters, and to continuously measure and record them.

Any process variable can be controlled manually or in a local automatic mode as well as by a computer programme. The computing system includes the control computer, operator's panel (display terminal), alphanumeric printer, and other devices, of which the operator's panel and alphanumeric printer are arranged in direct proximity to the plant instrumentation and automatic control facilities for the operator to communicate with the control computer. The plant data are fed into the computing system which performs all the neces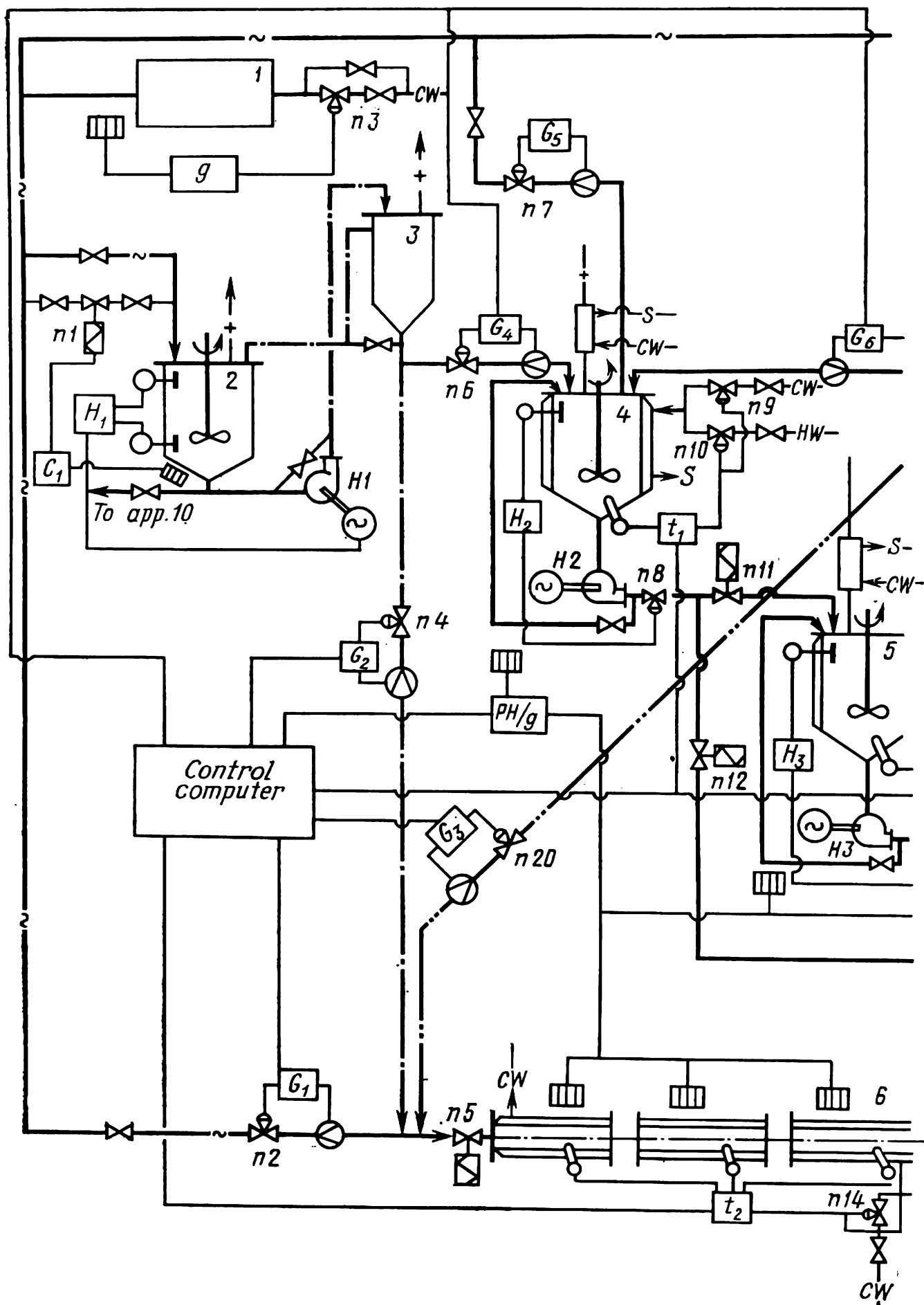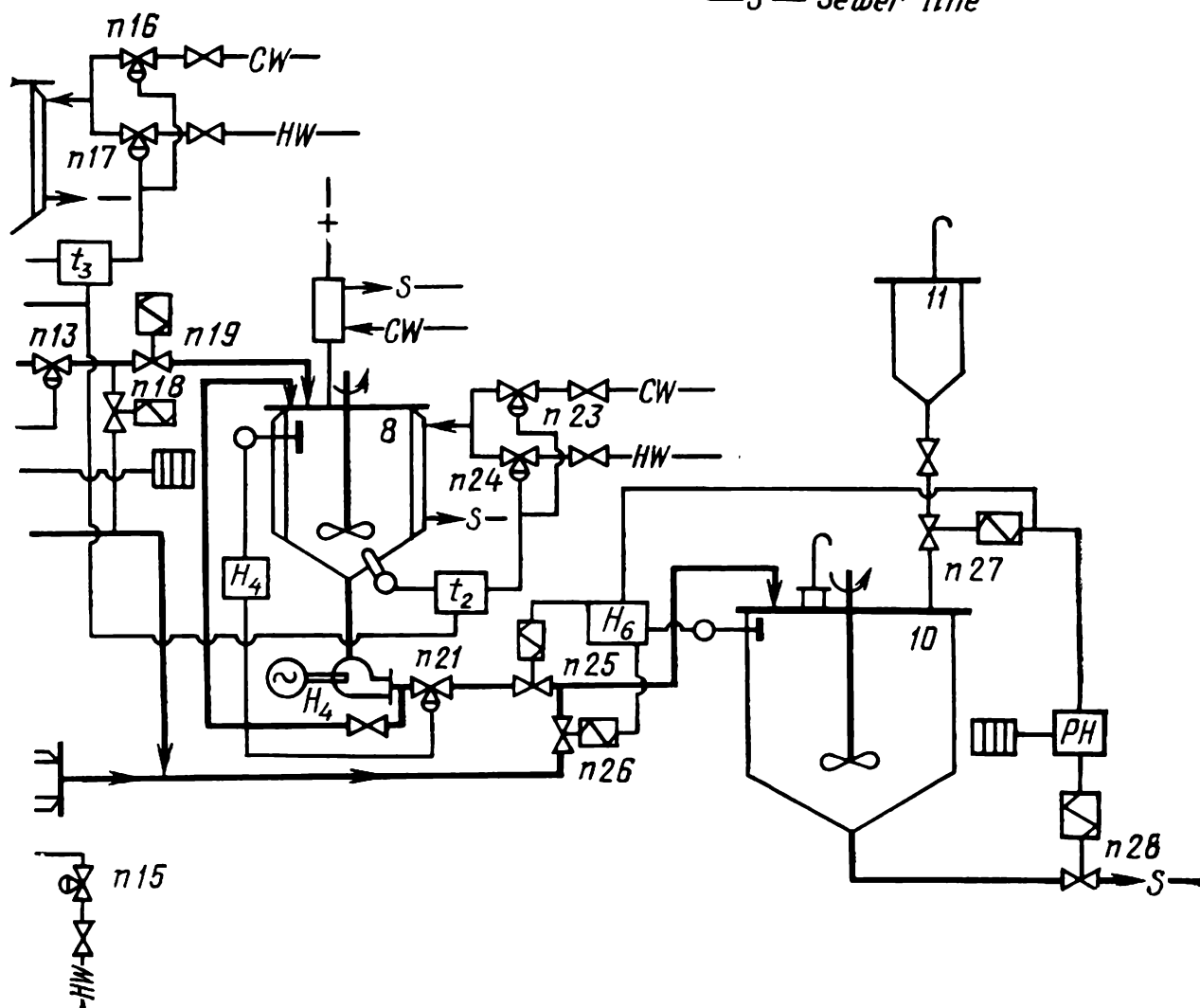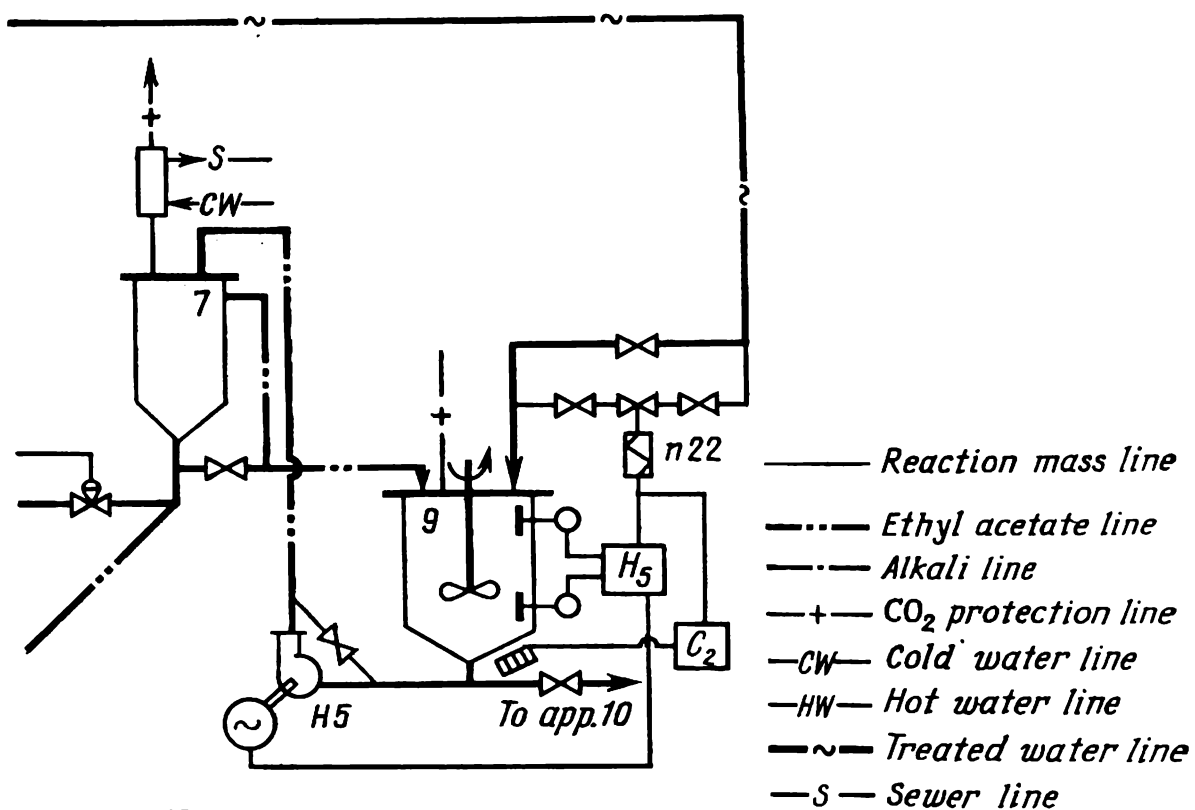sary computations, selects the appropriate model, and corrects its parameters. The computing system can also perform the function of the operator's consultant in optimizing the process and control it under optimal conditions in off-line mode. The operator's panel enables presentation of any current and/or computed values or model correction factors on the digital display. The operator can change the correction factors from the panel or initiate other modes of the control computer operation. The printer permits single-action and line-a-time printout of the wanted information in the alphanumeric or graphic form. The single-action mode is used mostly for printing out critical deviations of variables from the specified values, owing to its inherently high speed and the possibility of printing in two colours.

The plant for homogeneous noncatalytic saponification of ethyl acetate with sodium hydroxide (Fig. 74) represents a cascade of three reactors *4*, *5*, and *8*, capable of operating intermittently, continuously, and in series with intensive mixing, plus a plug-flow reactor *6*.

Each reactor in the cascade has a jacket, a mechanical stirrer, and a reflux condenser. The reaction mass is delivered from the cascade reactors by centrifugal pumps ($H2$, $H3$, $H5$), while from the plug-flow reactor it flows by gravity. The same pumps drive the reaction mass through the transducers of the instruments for measuring the physicochemical parameters. They can also be used for recirculation.

The automated plant also comprises a water treatment unit *1*, service tanks *2*, *9* and overhead tanks *3*, *7* for sodium hydroxide and ethyl acetate, respectively, a neutralizing well *10* for the reaction products, and a tank *11* for acid. The water treatment unit *1* performs filtration and removes various impurities with the aid

of ion-exchange resins to purify water and minimize its conductivity in view of the fact that one of the process variable measuring techniques is based on changes in conductivity. The conductivity of the water flowing from the water treatment unit serves as an indicator of its performance. When the conductivity increases, the valve $n3$ controlled by a conductivity apparatus reduces the water flow rate, thereby ensuring its quality. Water flows from the treatment unit *1* into the tanks *2* and *9* for preparation of the sodium hydroxide and ethyl acetate solution. The tank *2* receives a weighed amount of solid sodium hydroxide through the charging hole. The tank *9* is filled with a precalculated and measured amount of ethyl acetate. The tanks accommodate electrically driven mechanical stirrers.

As the sodium hydroxide is being dissolved and water added, the conductivity of the solution changes. As soon as a particular value of conductivity, corresponding to the predetermined concentration of the solution, is reached, the water supply into the tank *2* is automatically cut off by the valve $n1$. If a mistake has been made (too much of sodium hydroxide has been charged) or, for some other process-related reasons, the solution in the tank exceeds the permissible upper level, the level controller H may also cut off the water supply into the tank *2* by means of the same valve $n1$. The prepared alkali solution is delivered from the tank *2* by the centrifugal pump $n1$ into the constant-level overhead tank *3* from which it may flow at a specified constant rate into the first reactor *4* of the cascade and into the plug-flow reactor *6*.

The constant flow rate of the alkali through the reactors is maintained by flow controllers G_1 and G_2 actuating final-control valves ($n6$ and $n4$). The ethyl acetate flow rate is controlled in a similar fashion. The reactors receive pure water from the water treatment unit at specified constant rates maintained by the flow controllers G_1 and G_2 and final-control valves ($n2$, $n7$).

The required volume of the reaction mass in any reactor of the cascade is maintained independently with the aid of level controllers h_2, h_3, and h_4, as well as final-control valves $n8$, $n13$, and $n21$. The desired temperature can be maintained in any reactor independently by means of temperature controllers t_1, t_2, t_3, and t_4 and final-control valves $n9$, $n10$, $n14$, $n15$, $n16$, $n23$, and $n24$ mounted on the lines feeding cold and hot water into the reactor jackets. The reactors are designed to operate under the following conditions: reactor *4*—perfectly mixed, operating intermittently, semicontinuously, and continuously; reactors *4* and *5*—two perfectly mixed, operating continuously in series; reactors *4*, *5* and *8*—three perfectly mixed reactors operating continuously in series; and reactor *6*—operating under plug-flow conditions. These conditions are maintained

by solenoid valves $n5$, $n11$, $n12$, $n18$, and $n19$ controlled from the panel.

The conversion is monitored by automatic conductivity apparatus and pH meters. The reaction products from the reactors *4, 5, 6, 8* and the starting substances from the tanks *2, 9* are delivered into the neutralizing well *10* in which they may accumulate. In the neutralizing well provision is made for (a) an electrically driven mechanical stirrer intended to intensify the neutralization process; (b) a circuit for automatic level indication (H_6) and cut off of the drain tank by means of the valves $n25$ and $n26$ to avoid overflow; and (c) an automatic pH meter for neutralization of the effluents, which controls the valve $n27$ feeding acid from the tank *11* and, after the pH value is brought to *7*, the valve $n28$ for automatic disposal of the acid into the drain system. The tasks accomplished at the plant include determination of the ester saponification rate constant, activation energy of this reaction, and the temperature-independent factor in the Arrhenius equation; selection and computation of the reactor operating conditions, using the previously derived kinetic parameters; studying the effect of the reactor hydrodynamics on its performance; and comparison of the performance characteristics of reactors of different types.

1. DETERMINATION OF THE KINETIC CONSTANTS OF THE REACTION OF ETHYL ACETATE SAPONIFICATION WITH SODIUM HYDROXIDE

The tasks to be accomplished at this point include: (a) determination of the mean value of the reaction rate constant; (b) calculation of the apparent activation energy and temperature-independent factor in the Arrhenius equation; and (c) determination of the reaction order.

The process is conducted in the reactor *4* (Fig. 74) operating intermittently. It is charged with a calculated amount of an aqueous solution of sodium hydroxide, the specified temperature being preset by the instrument. Ethyl acetate can be introduced into the reactor only after the temperature has remained stable for 10 to 15 minutes. At the same time, a stopwatch is started or the chart paper of the conductivity apparatus is marked, and this moment is considered as the onset of the reaction. The conductivity is measured immediately after mixing. The first four or five measurements are taken at intervals not longer than a minute, the next two or three are taken at 1.5- to 2-min intervals, another five measurements are taken after three minutes and, finally, measurements are taken at five minute intervals for an hour. The measurement results are tabulated as follows:

Initial sodium hydroxide concentration C_{0NaOH}, mole/dm³ ...
Initial ethyl acetate concentration $C_{0\,ea}$, mole/dm³ ...
Experimental temperature, °C ...
Conductivity constants n for the vessel ...
Conductivity $\varkappa_0$, ohm⁻¹·cm⁻¹ ...

Elapsed time τ, min	Solution resistance R_x, ohm	Current conductivity of solution $\varkappa_\tau$, ohm⁻¹·cm⁻¹	Current concentration of CH₃COO⁻ ions (salt, alcohol concentration) C_x, mole/dm³	Reaction rate constant k, mole/dm³·min
				$k_{mean} =$

The experiment is repeated at a different temperature. The mean value of reaction rate constants is calculated using Eq. (3.40). The results of two experiments are used to calculate the activation energy from

$$E = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1}. \qquad (3.57)$$

Solution of the Arrhenius equation (3.44) with respect to k_0 gives the value of the temperature-independent factor. The report must include: (a) plots of kinetic curves; (b) a plot showing log u as a function of log C; and (c) conclusions based on analysis of the calculations and plots. It must also be proved that the reaction is of the second order.

2. ANALYSIS OF A BATCH PLUG-FLOW REACTOR

This part of the work deals with the kinetics of the ethyl acetate saponification reaction, kinetic regularities of the reaction for selection and calculation of the reactors, and the effect of the reactor hydrodynamics on the process variables.

The procedures of this work are similar to those of the previous one with the difference that the experiment is conducted at a single temperature with the results of the previous work being used.

The current ethyl acetate concentration is calculated using the experimental data with due account for the initial concentration of ethyl acetate and its amount entering into the reaction and on the basis of Eq. (3.48). The amount of ethyl acetate is equivalent to that of the reacted sodium hydroxide.

The results are tabulated as follows:

Total solution volume v, dm³ ...
Initial sodium hydroxide concentration $C_{0\,NaOH}$, mole/dm³ ...
Initial ethyl acetate concentration $C_{0\,ea}$, mole/dm³ ...
Experimental temperature, °C ...

Elap-sed time τ, min	Solu-tion resist-ance R_x, ohm	Current conductiv-ity of solution $\varkappa_\tau$, ohm⁻¹× ×cm⁻¹	Current NaOH con-centration in solution C_{NaOH}, mole/dm³	Current ethyl acetate concen-tration C_{ea}, mole/dm³	Percent-age con-version		Reaction rate u, mole/(dm³× ×min)	k, mole/(dm³× ×min)
					x_{NaOH}	x_{ea}		
								$\vdots$
								k_{mean}

In addition to the above tables and calculations, the report must include: (1) determination of the effect of temperature on the reaction rate; (2) determination of the following relations at a constant temperature

$$u = f(\tau), \quad u = f(C_{NaOH}), \quad u = f(x_{NaOH});$$

(3) determination of the dependence of the reactor capacity on the conversion of sodium hydroxide or ethyl acetate and the time spent on unproductive operations. The reactor capacity is calculated using the formula

$$G = m/(\tau_r + \tau_{aux}), \tag{3.58}$$

where G is the reactor capacity with respect to one of the reaction products (sodium acetate, ethanol), in mole/h; m is the amount of the sodium acetate or ethanol produced per operation; τ_r is the working time (reaction time); and τ_{aux} is the auxiliary time (time spent on such unproductive operations as charging and discharging of the reagents, startup and shutdown of the reactor), in h; (4) calculation of the percentage conversion of sodium hydroxide (ethyl acetate) in the batch reactor at specified temperature, residence time and initial sodium hydroxide (ethyl acetate) concentrations; (5) calculation of the time of residence of the reagents in the batch reactor, necessary to achieve the desired conversion of sodium hydroxide (ethyl acetate) at known temperature and initial concentrations of sodium hydroxide (ethyl acetate); (6) determination of the reactor size in terms of ca-pacity and reagent residence time; (7) $C_{NaOH} = f(\tau)$, $x_{NaOH} = f(\tau)$, $u = f(\tau)$, $u = f(C_{NaOH})$, and $u = f(x_{NaOH})$ curves or similar relations for ethyl acetate; (8) conclusions based on analysis of the calculations and plots; and (9) recommendations concerning the optimal conditions.

3. ANALYSIS OF A CONTINUOUSLY OPERATING
TUBULAR PLUG-FLOW REACTOR

In this part of the work, students must (1) apply the kinetics of chemical reactions to selection and calculation of the reactors and (2) study the effect of the reactor hydrodynamics on the process variables.

Used in the experiment is the reactor *6* (see Fig. 74) into which the reagents flow by gravity from the overhead tanks *3* and *7*. The reagent flow rates are adjusted by flow controllers G_1, G_2, and G_3 and respective valves *n*2, *n*4, and *n*20. The specified temperature is maintained by means of the temperature controller t_2 and valves *n*14 and *n*15.

To measure concentrations along the reactor length transducers are provided operating in conjuction with respective instruments, which permits the process to be continuously monitored with sampling. The concentration variation data are used in the performance analysis of the continuous tubular reactor in accordance with the assignment.

The initial concentrations of sodium hydroxide and ethyl acetate at the reactor inlet are calculated from the reagent concentrations in the initial solutions and the ratio of their flow rates. The reactor volume is calculated using the formula

$$v = 0.785 \ D^2 l, \tag{3.59}$$

D being the internal diameter of the reactor, in m.

The time of residence of the reagents in the reactor is defined as

$$\tau = v/v_1,$$

where v is the reactor volume, in m³, and v_1 is the reagent flow rate, in m³/h.

The assignment includes determination of changes in concentration and conversion of sodium hydroxide and ethyl acetate over the reactor length at a constant temperature. The sodium hydroxide to ethyl acetate ratio may be 1 : 1, 1 : 2, 1 : 3, or 1 : 4. The reagent ratio is varied from 1 : 1 to 1 : 4 without changing the overall reagent flow rate. The next step is plotting of the kinetic curves $C_{NaOH} = f(\tau)$, $C_{NaOH} = f(l)$, $x_{NaOH} = f(\tau)$, $x_{NaOH} = f(l)$, $u = f(C_{NaOH})$, and $u = f(x_{NaOH})$, or similar curves for ethyl acetate. The experiments are carried out at a constant ratio between the sodium hydroxide and ethyl acetate volumes (1 : 1, 1 : 2, 1 : 3, or 1 : 4) and at a reagent flow rate variable at equal intervals or a multiple one. The time of residence of the reagents in the reactor is determined theoretically, which is necessary to attain the desired percentage conversion at known temperature and initial reagent concentrations, using the values of the rate constant, activation energy, and tem-

perature-independent factor, derived during the experiments described in Parts 1 and 2 of this work. The calculated values are compared with the experimental data. Also calculated are the concentrations and percentage conversions of sodium hydroxide and ethyl acetate over the length of the plug-flow reactor at known temperature, initial sodium hydroxide and ethyl acetate concentrations, and reagent flow rate. Again, the calculated values are compared with the experimental data. The reactor size is determined from the specified residence time and reagent flow rate. The experiments are conducted at different temperatures, and the effect of temperature on the process variables is determined.

The measurement results are tabulated as follows:

Sodium hydroxide solution flow rate, dm^3/h ...
Ethyl acetate solution flow rate, dm^3/h ...
Overall reagent flow rate, dm^3/h ...
Initial NaOH concentration C_0 at the reactor inlet, $mole/dm^3$ ...
Initial ethyl acetate concentration C_0 at the reactor inlet, $mole/dm^3$ ...
Experimental temperature, °C ...

Distance from reagent mixing point to measurement point l, cm	Reactor volume from inlet to measurement point v_r, cm^3	Reagent residence time τ, h	Solution resistance R_x, ohm	Concentration, $mole/dm^3$		Percentage conversion	
				C_{NaOH}	C_{ea}	x_{NaOH}	x_{ea}

In addition to the above table and calculations, the report must include: (a) plots; (b) conclusions based on analysis of the calculations and plots; and (c) recommendations concerning the optimal operating conditions.

4. ANALYSIS OF A CONTINUOUS PERFECTLY MIXED REACTOR AND A CASCADE OF PERFECTLY MIXED REACTORS ARRANGED IN SERIES

This part of the work includes the following steps: (1) using the kinetics of the chemical reactions to select and calculate the reactors; (2) studying the effect of the reactor hydrodynamics on the process variables; and (3) comparing the characteristics of batch, plug-flow and perfectly mixed reactors.

The accomplishment of these tasks requires the results of the experiments described in Parts 1 through 3 of this work.

The experiment is based on the reactors *4, 5*, and *8* (see Fig. 74) operating in series in a cascade consisting of two or three reactors, or the perfectly mixed reactor *4*. The initial concentrations of

sodium hydroxide and ethyl acetate at the reactor inlet are calculated from those of the reagents in the initial solutions and the ratio of their flow rates. The characteristic equation for a perfectly mixed reactor, with respect to one of the components, is

$$\tau = v/V_1 = C_{A_0} x_{A_f}/u_{A_f}, \qquad (3.60)$$

where v is the volume of a single perfectly mixed reactor, V_1 is the reagent flow rate, and x_{A_f} is the final percentage conversion of a component.

In the calculations involving a cascade of perfectly mixed reactors, the following characteristic equation is used:

$$\tau = v/V_1 = (m/k) [(C_1/C_f)^{1/m} - 1]. \qquad (3.61)$$

First, the concentrations of sodium hydroxide and ethyl acetate at the outlet of the reactors *4, 5,* and *6* (see Fig. 74) are determined at a constant temperature. Then, the percentage conversions in a respective reactor and at each cascade stage are calculated. The sodium hydroxide to ethyl acetate ratio may be 1 : 1, 1 : 2, 1 : 3, or 1 : 4. Without changing the overall flow rate of the reagents, their ratio is varied from 1 : 1 to 1 : 4. $C_{NaOH} = f(\tau)$, $x_{NaOH} = f(\tau)$, or $C_{ea} = f(\tau)$, $x_{ea} = f(\tau)$ curves are plotted at a constant temperature for each cascade stage. The experiments are carried out at a constant ratio between the sodium hydroxide and ethyl acetate volumes (1 : 1, 1 : 2, 1 : 3, or 1 : 4), at a reagent flow rate varying at equal intervals or a multiple one. The reagent residence time is calculated, which is necessary to achieve the specified percentage conversion at known temperatures and initial reagent concentrations, using the rate constant, activation energy, and other data derived in the experiments described in Parts 1 and 2 of this work. The calculated values are compared with the experimental data. Also calculated are the concentrations and percentage conversions of sodium hydroxide and ethyl acetate at each cascade stage, at known temperature, initial sodium hydroxide and ethyl acetate concentrations, and reagent flow rate. The calculated values are again compared with the experimental data. The cascade reactor sizes are defined in terms of the specified residence time and reagent flow rate. The experiment is conducted at different temperatures. The effect of temperature on the process variables is determined. The capacities of plug-flow, perfectly mixed and batch reactors are compared. Also compared is the total reaction volume of the cascade with that of a single perfectly mixed reactor, other operating conditions being the same.

The results are tabulated as follows:

Initial sodium hydroxide concentration C_{NaOH}, mole/dm³ ...
Initial ethyl acetate concentration, C_{ea}, mole/dm³ ...
Sodium hydroxide solution flow rate, dm³/h ...
Ethyl acetate solution flow rate, dm³/h ...
Overall reagent flow rate, dm³/h ...
Experimental temperature, °C ...

Reagent residence time τ, min	Solution resistance at reactor outlet R_x, ohm	Concentration, mole/dm³		Percentage conversion	
		C_{NaOH}	C_{ea}	x_{NaOH}	x_{ea}

In addition to the above table and calculations, the report must include: (a) $C_{NaOH} = f(\tau)$, $x_{NaOH} = f(\tau)$, $C_{NaOH} = f(m)$, $x_{NaOH} = f(m)$, $u = f(C_{NaOH})$, and $u = f(x_{NaOH})$ curves, or similar relations for ethyl acetate; (b) conclusions based on analysis of the calculations and plots; and (c) recommendations concerning the optimal operating conditions.

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Kafarov, V. V., *Cybernetic Methods in Chemistry and Chemical Engineering*, Moscow, 1971.

Chemical Technology, Mukhlyonov, I. P., Averbukh, A. Ya., Tumarkina, E. S., *et al.*, Moscow, 1977.

Instructions to the Laboratory Work "Performance Analysis of Liquid-Phase Reactors"

1. Study the experimental plant and procedure.
2. Check the plant layout.
3. Prepare the sodium hydroxide solution, wearing rubber gloves and goggles.
4. Start the plant and carry out the experiment only under the instructor's supervision and according to his assignments.
5. Take all the safety precautions applicable to chemical laboratories, with particular attention to the characteristics of the substances used.

Characteristics of the Substances Used

Ethyl acetate—colourless inflammable liquid (molecular weight 88.1) with a pleasant specific odour: melting point, 82.4°C; boiling point, 77.1°C; density $d^{20} = 0.900$. When ethyl acetate is present in a mixture with air in an amount of 2.2 to 11.4 vol.%, the mixture becomes explosive. The maximum permissible concentration (MPC) of ethyl acetate vapours in air is 200 mg/m³.

Sodium hydroxide—white solid substance readily soluble in water, glycerine, and alcohol. Solid sodium hydroxide binds water and absorbs carbon dioxide from air (molecular weight 40.0): melting point, 320°C; boiling point, 1390°C; MPC = 0.5 mg/m³. While preparing the solution, one must wear rubber

gloves because sodium hydroxide affects the skin on which a soft crust may form, not preventing the alkali from penetration into deeper tissues.

Ethanol—highly inflammable colourless liquid (molecular weight 46.07): melting point, 114.15°C; boiling point—78.39°C; density, $d_4^{15} = 0.793$. The range of inflammation in a mixture with air is 3.6 to 14 vol.%. MPC, 1000 mg/m^3. Ethanol is miscible with water at any ratios.

LABORATORY WORK 23. OPTIMIZATION OF A CONTACT PLANT OF SULPHURIC ACID, OPERATING ON A DOUBLE CONTACT-DOUBLE ABSORPTION PRINCIPLE

In this work, a contact plant for oxidation of sulphur dioxide in the production of sulphuric acid is used as an example illustrating the main steps of optimization of the performance of catalytic reactors.

At present, powerful industrial systems with double contact and double absorption (DC/DA) form the basis of sulphuric acid manufacture. The presence of two contact and absorption steps after the first stage permits the overall sulphur dioxide conversion to be brought up to 99.6-99.8%, whereas in single-step systems the conversion is only up to 98%.

In its simplified form, the DC/DA process comprises the following steps: production of gas from the sulphur-containing stock, its purification, first-stage oxidation of SO_2, first absorption of SO_3, final oxidation of SO_2 at the second stage, and second absorption of SO_3. It is precisely the provision for the first absorption abstracting the major amount of SO_3 from the reacted gas that ensures high percentage conversion in the system as a whole.

The optimal process conditions are ensured by the contact plant, which is why this work deals exclusively with selection of optimal operating conditions of the contact plant. The optimization criterion in this case is the maximum final conversion at given process variables, such as gas flow rates, initial concentration of sulphur dioxide and oxygen, and catalyst bed height. The maximum final degree of oxidation is, in turn, achieved by selection of appropriate temperatures in the catalyst beds.

Laboratory conditions impose their own specific on the selection of initial variables because it is difficult to change the reactor diameter and catalyst bed height in the laboratory. Therefore, this work boils down essentially to optimization of an existing rather than newly designed system. Nevertheless, the results can be applied to the latter as well.

The contact plant in DC/DA systems comprises two catalytic reactors and may be designed in two versions: (1) the first and second stages include catalytic reactors with fixed beds; (2) the first stage incorporates a reactor with the catalyst being in fluidized beds,

while the reactor of the second stage has fixed catalyst beds. The second type is more universal for it permits processing gases with high concentrations of SO_2 as well as dust-laden gases. This is precisely why considered in this work is a DC/DA system with a fluidized-bed reactor in the first stage. The physicochemical aspects of the process of SO_2 oxidation to SO_3 were treated in Work 13.

To study the optimal operating conditions of the contact plant calls for development of mathematical models of the reactors. If a fixed-bed reactor is described by a plug-flow model, the models corresponding to a fluidized-bed reactor are more complex and include parameters difficult to calculate. These parameters are reliably determined in special studies involving a "cold" model of a fluidized-bed reactor. Therefore, the present work is divided into three parts: (1) derivation of the parameters of equations describing a fluidized-bed reactor in a cold model; (2) examination of the optimal operating conditions of the contact plant, using mathematical models based on the parameters derived according to (1); and (3) experimental studies of the optimal operating conditions at a DC/DA plant.

1. BASIC CONCEPTS OF THE FLUIDIZED BED AND INITIAL PARAMETERS OF THE MATHEMATICAL MODEL OF A FLUIDIZED-BED REACTOR

A fluidized bed can be created in a column with a gas distributing device, the gas being blown from down upward through a bed of a fine-grained material. As the gas velocity increases, the hydraulic resistance of the stationary bed grows at first, following the curve AB (Fig. 75), then, at a particular point in time, the weight of the particles is counterbalanced by the upward thrust of the rising current, and the bed becomes suspended over the curve portion BC, its resistance being independent of the gas velocity (portion CE) for the rest of the time till particles start being entrained. The slight rise of the curve (portion BC) is due to the gas energy being spent in loosening the bed. When the bed is brought from the suspended

Fig. 75. Experimental determination of the fluidization onset velocity

(fluidized) to a stationary state, no such rise is observed (curve CD). The minimal gas velocity at which the hydraulic resistance of the bed becomes independent of the gas velocity is known as the suspension or fluidization onset velocity. This velocity (w_f) is determined

experimentally from the relationship between the bed resistance ΔP_{bed} and gas velocity w or calculated using appropriate formulas. The most universal formula is

$$\text{Re}_f = \frac{\text{Ar}}{1400 + 5.22\,(\text{Ar})^{0.5}}, \qquad (3.62)$$

where $\text{Re}_f = \frac{w_f d}{\nu}$ is the Reynolds criterion; $\text{Ar} = \frac{g d^3}{\nu^2} \cdot \frac{\rho_s - \rho_g}{\rho_g}$ is the Archimedes number; ν is the kinematic viscosity coefficient of the gas; g is the free fall acceleration; and ρ_s, ρ_g stand for the densities of the solid particles and gas, respectively.

In defining the hydrodynamic conditions it is customary to resort to the difference between the working velocity across the entire bed and the fluidization onset velocity ($\Delta w = w - w_f$) or the fluidization number

$$W = w/w_f. \qquad (3.63)$$

The fluidized bed is characterized by inhomogeneities, or gas bubbles and channels variable in time and in space.

The hydrodynamics of the fluidized bed is studied in cold models of reactors, which are essentially cylindrical columns with transparent walls or large viewing windows. Fig. 76 represents cinema frames of the upper portion of a fluidized bed in a cold model. Studying the bed structure in a three-dimensional apparatus involves technical difficulties (e.g., X-ray cinematography). Therefore, the processes of formation and development of inhomogeneities in the bed are analyzed in the so-called planar (two-dimensional) model in which one of the cross-sectional dimensions of the bed is small, whereby its internal structure can be observed.

The cinema frames of Fig. 77 show a fluidized bed in a planar model. The effect of the gas velocity on the bed inhomogeneity can be clearly seen. At low velocities (Fig. 77a, b), single bubbles of small size rise in the bed. At high velocities (Fig. 77c, d), movement of solid particle aggregates becomes visible. In the case of solid particles 0.2 to 4 mm in diameter, the hydrodynamic conditions at $\Delta w \leqslant 0.2$ m/s are known as bubbling. At $\Delta w \geqslant 0.6$ m/s we are dealing with what is referred to as aggregation. Planar model studies give a good insight into the physics of the phenomena occurring in the fluidized bed. Observations of a planar model allow the fluidized bed under bubbling conditions to be defined in terms of bubble size, number and ascending speed. In the case of aggregation, when voids in the bed are highly deformed and unstable in time, the bed characteristics may include the void, or gas, volume φ and the surface separating the dense matter from voids, or interfacial area, f. These characteristics are also applicable to the bubbling conditions.

(a)   (b)

(c)
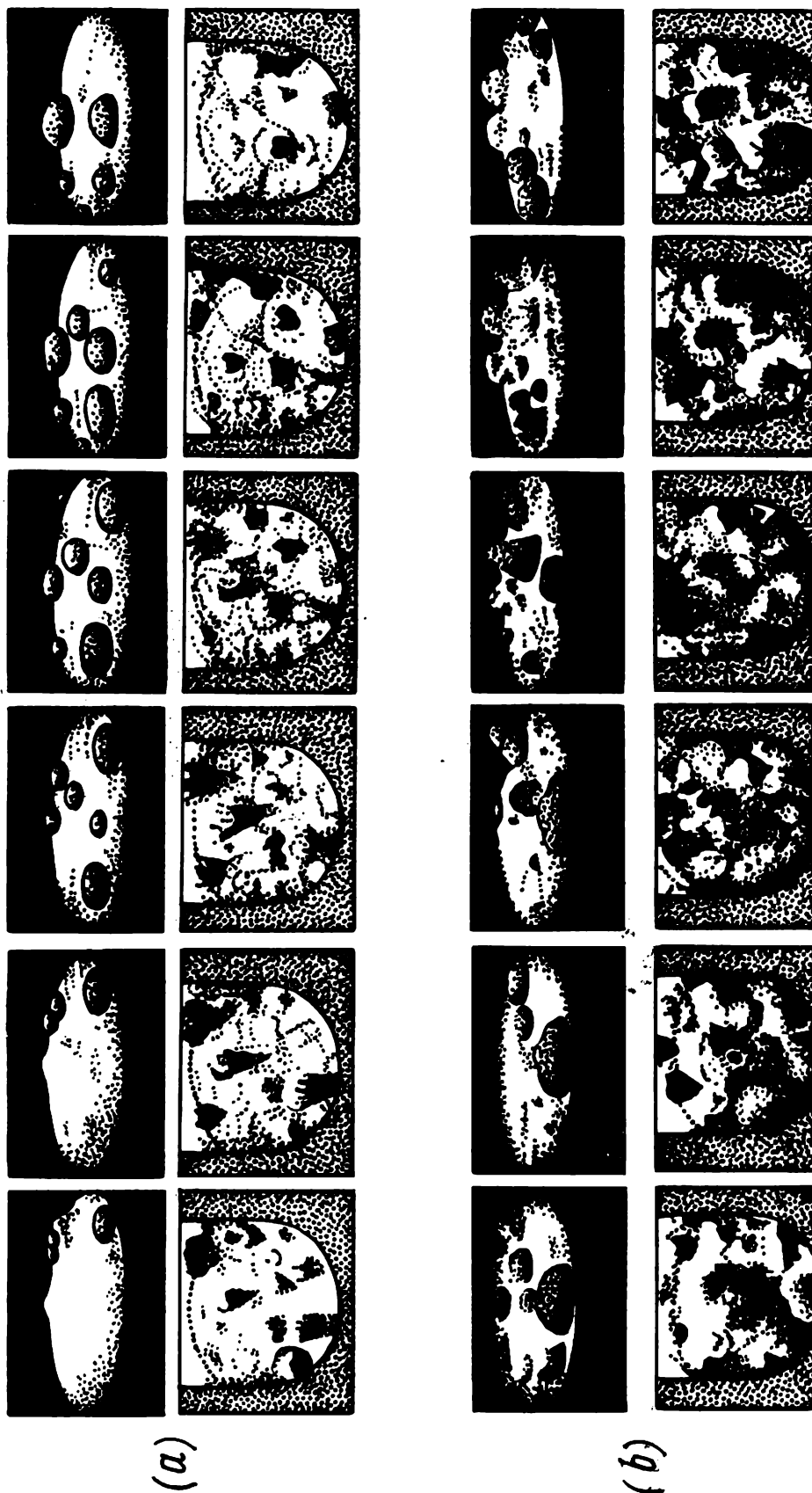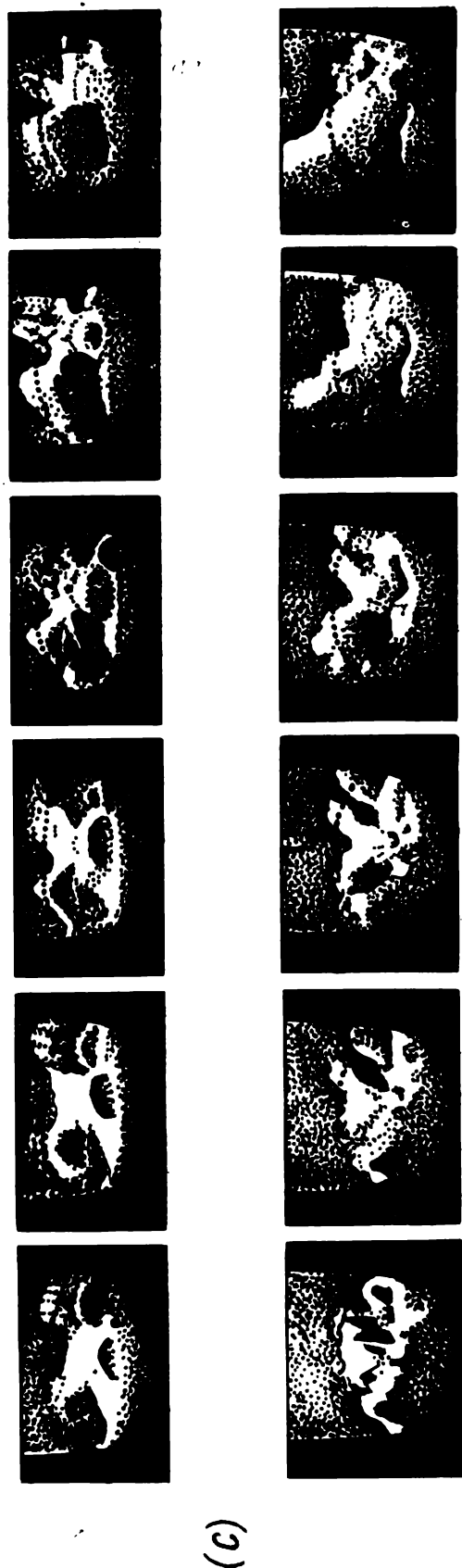
Fig. 76. Cinema frames of the upper portion of a fluidized bed in a cold model; bed height $H_0 = 0.2$ m, aluminosilicate with an average particle size $d = 0.75$ mm:

a—$\Delta w = 0.05$ m/s; b—$\Delta w = 0.1$ m/s; c—$\Delta w = 0.2$ m/s; d—$\Delta w = 0.4$ m/s

Fig. 77. Cinema frames of a fluidized bed in a planar model; bed height $H_0 = 0.4$ m, alumino-silicate with an average particle size $\bar{d} = 1.5$ mm:

a—$\Delta w = 0{,}15$ m/s; b—$\Delta w = 0{,}4$ m/s; c—$\Delta w = 1{,}2$ m/s; d—$\Delta w = 2{,}0$ m/s

The bed structure in a three-dimensional model can be defined in the same qualitative terms. The relation $\overline{\Delta P}_{bed} = f(w)$ curve shown in Fig. 75 is idealized. In a real bed, the instantaneous value of the pressure drop (ΔP_i) is variable in time and fluctuates around
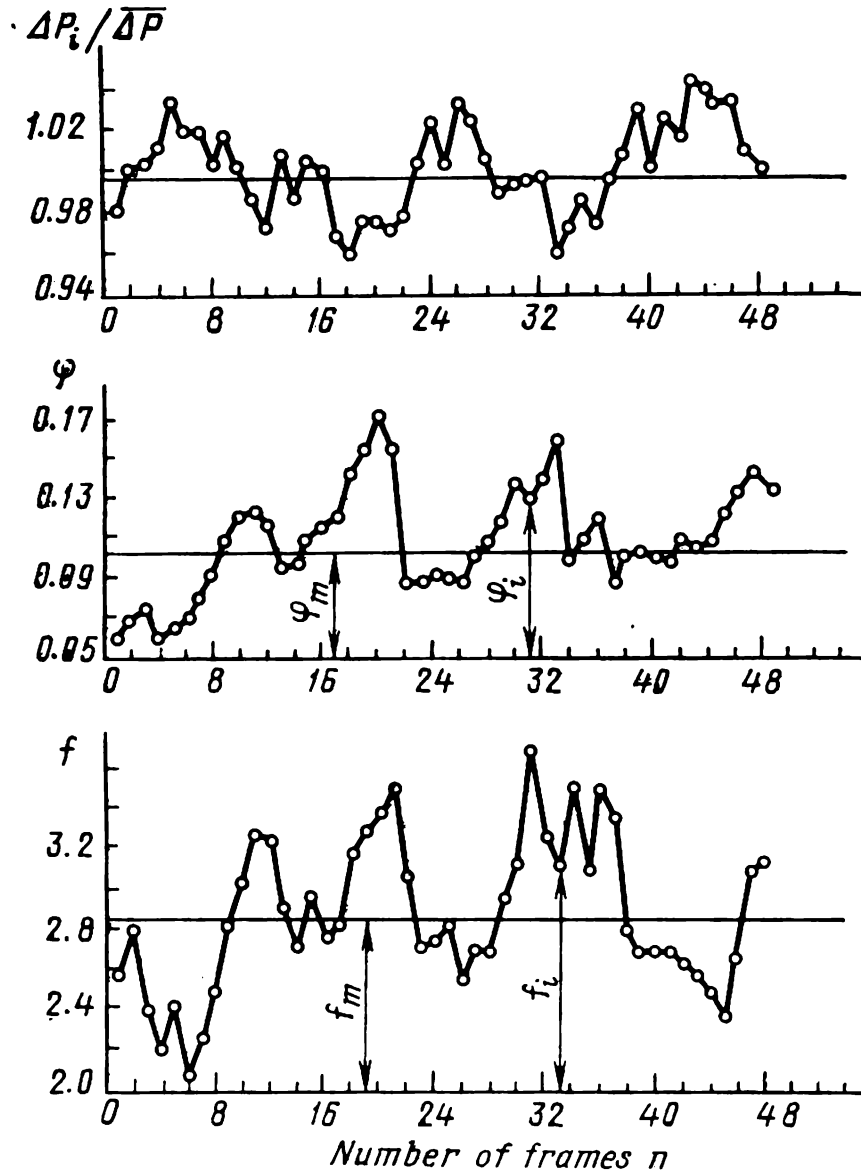
Fig. 78. Time variations of structural parameters and pressure drop fluctuations. Filmed at a speed of 24 frames per second

the mean value $\overline{\Delta P}_{bed}$. The amplitude and frequency of fluctuations in ΔP_i depend on Δw, the initial bed height H_0, solid particle diameter d, and are determined by the non-stationari y of gas flows through different points of the bed. Therefore, the temporal behaviour of ΔP_i is indicative of the internal structure of the bed. An example of variations in ΔP_i with f and φ for a planar model is illustrated in Fig. 78.

The overall pressure drop across the bed provides integrated characteristics which are not always sufficient. If the points at which the

pressure drop across the bed is measured are marked, one can describe the fluctuations in the pressure drop, caused by redistribution of gas flows and absolute pressures around a bubble. Hence the local structural characteristics, such as bubble size and ascending speed, which are included in the mathematical models of fluidized-bed reactors— their determination is important for practical calculations. Therewith, distinction is made between axial pressure drop fluctuations, when the measurement points are arranged in a single vertical plane, and radial fluctuations, when the measurement points lie in a horizontal plane.

The fluctuation amplitude and frequency are dependent on the gas velocity, bed height, and axial coordinate, the amplitude increas-
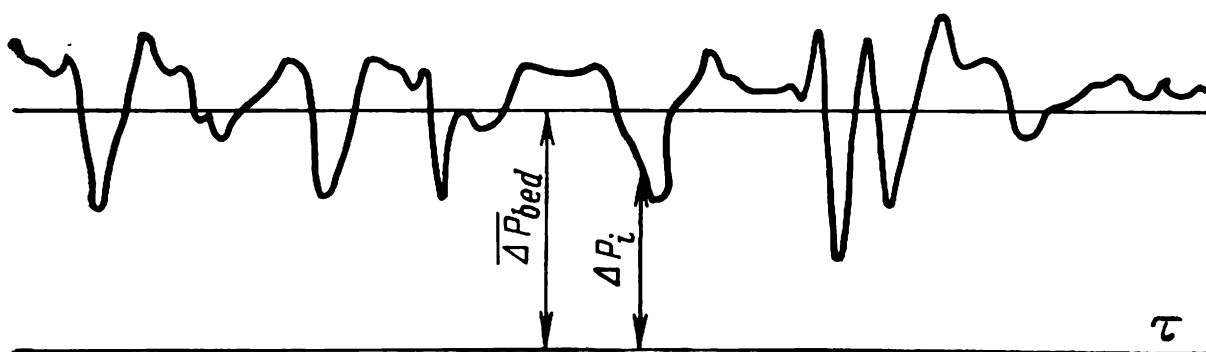
Fig. 79. Time variations of pressure drop across the bed

ing with the velocity and coordinate as a result of bubble growth. Fig. 79 represents a typical oscillogram of pressure fluctuations. Pressure fluctuations, which are essentially a random stationary ergodic process, are characterized by the mean value $\overline{\Delta P}_{bed}$, relative (ψ) and absolute $(\overline{\Delta\Delta P})$ deviations from the mean value $\overline{\Delta P}_{bed}$, variances D, correlation function $K(m)$, and differential distribution of amplitudes $P(\Delta\Delta P)$ and frequencies $P(\omega)$. The mean value of pressure drop is

$$\overline{\Delta P}_{bed} = \frac{1}{n} \sum_{i=1}^{n} \Delta P_i, \qquad (3.64)$$

where n is the number of values ΔP_i; the mean relative deviation is

$$\psi = \frac{\overline{\Delta\Delta P}}{\overline{\Delta P}_{bed}} = \frac{1}{n\overline{\Delta P}_{bed}} \sum_{i=1}^{n} |\Delta P_i - \overline{\Delta P}_{bed}|; \qquad (3.65)$$

and the standard deviation is

$$\sigma = \left[\frac{1}{n-1} \sum_{i=1}^{n} (\Delta P_i - \overline{\Delta P}_{bed})^2 \right]^{1/2}. \qquad (3.66)$$

The instantaneous values of the differential pressure drop between two measurement points take the form

$$\Delta P_{d_i} = \left(\frac{\Delta P_i}{\overline{\Delta P_{bed}}}\right)_1 \overline{\Delta P_1} - \left(\frac{\Delta P_i}{\overline{\Delta P_{bed}}}\right)_2 \overline{\Delta P_2}, \qquad (3.67)$$

where $\overline{\Delta P_1}$ and $\overline{\Delta P_2}$ are the mean values of pressure in real units at the 1st and 2nd measurement points.

Eqs. (3.64) through (3.66) are also used to calculate, for the differential pressure drop, the mean relative and absolute deviations as well as the standard deviation. The cross correlation function is

$$K_{cc}(m) = \frac{1}{\sigma_1 \sigma_2 (n-m)} \sum_{i=1}^{n-m} (\Delta P_i - \overline{\Delta P}_{bed})_1 (\Delta P_{i+m} - \overline{\Delta P}_{bed})_2, \qquad (3.68)$$

where m is the number of the correlation function coefficient and subscripts 1 and 2 correspond to the parameters for the 1st and 2nd pressure measurement points.

Formation of a gas bubble changes the pressure pattern in a certain region, which brings about axial and radial pressure drop fluctuations. The pressure pattern near a moving spherical bubble is given in cylindrical coordinates by the function

$$\Delta P(r, z, r_b) = -\alpha \left[z - \frac{r_b^3 z}{(r^2 + z^2)^{3/2}} \right], \qquad (3.69)$$

where r_b is the bubble radius, r is a radius vector, z is an axial coordinate, and α is the resistance coefficient.

Eq. (3.69) suggests that the bubble affects the pressure gradient throughout the bed. However, in a real bed the number of bubbles is great, and one can always distinguish a "visibility zone" near a pressure measurement point, in which a gas bubble having a predominant influence is always present. On the average, this region is in the form of a cylinder having a radius L and a height $2r_b$; the dimension L is determined by the number of bubbles passing through unit horizontal section of the reactor per unit time, that is the frequency response, and is proportional to the bubble radius:

$$L = (\omega/\pi N)^{1/2} = Kr_b, \qquad (3.70)$$

where ω is the fluctuation frequency, and K is a coefficient dependent on the permeability of the medium.

The mean value of the amplitude of axial pressure fluctuations is the result of space averaging of all possible amplitudes derived from Eq. (3.69), which is equivalent to the mean value $\overline{\Delta\Delta P}$ corresponding to successive passage of bubbles along all possible paths in the course of time:

$$\overline{\Delta\Delta P}_{ax}(r_b) = \frac{\alpha}{K^2} [2K + 1.25 - 2(K^2 + 1)^{1/2}] r_b. \qquad (3.71)$$

A similar space averaging in measuring the radial pressure drop between two points at a distance $D \geqslant 2L$ from each other gives the mean value of the radial fluctuation amplitude:
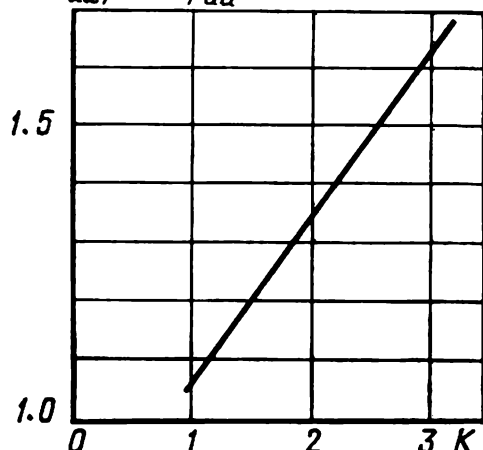
$$\Delta\Delta\overline{P}_{\text{rad}}\,(r_{\text{b}})|_{D \gg 2L} =$$

$$= \frac{3\alpha}{2K^3}\{\ln\,[K + (K^2 + 1)^{1/2}] +$$

$$+ K^2 - K\,(K^2 + 1)^{1/2} - 0.2\}\,r_{\text{b}}. \qquad (3.72)$$

The mean value of the radial pressure drop is zero since the average bed resistance at two points lying in a horizontal plane is the same.

The ratio between the mean absolute values of axial and radial fluctuations, obtained experimentally in real units, can be used to define the coefficient K in Eqs. (3.70) through (3.72) (Fig. 80). Substituting the derived value of K into Eq. (3.71) or (3.72), one can determine the mean bubble radius in the pressure measurement cross-section.

Fig. 80. $K = f\,(\overline{\Delta\Delta P_{\text{ax}}}/\overline{\Delta\Delta P_{\text{rad}}})$
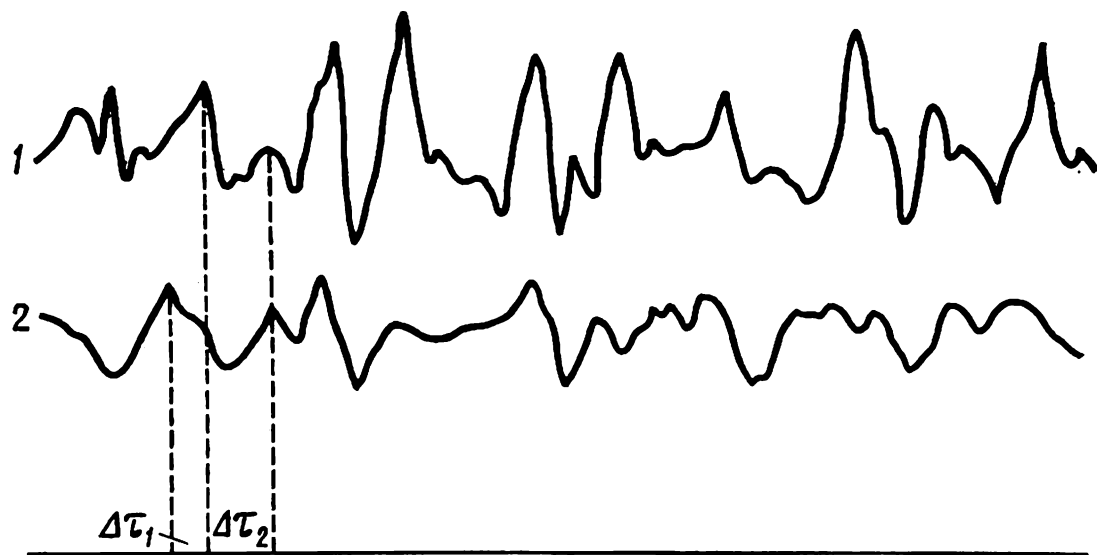
Fig. 81. Time lag:
1—lower transducer; *2*—upper transducer

A moving gas bubble successively affects the pressure at the measurement points aligned with the bed axis, with the result that the pressure varies with a time lag (Fig. 81). The time lag in pressure fluctuations occurs in the presence of a bubble and persists over a certain time $\Delta\tau_1$, while in the absence of a bubble the pressure varies within a single phase over time $\Delta\tau_2$.

The observed lag $\Delta\tau_{obs}$ is determined from the cross correlation function (3.68) represented graphically in Fig. 82. The true time lag associated with the bubble ascending speed is determined from the observed lag according to the equation

$$\Delta\tau_{true} = \Delta\tau_{obs}\frac{\Delta\tau_1 + \Delta\tau_2}{\Delta\tau_1} = \frac{'\Delta\tau_{obs}}{K_{cc}}, \qquad (3.73)$$

where K_{cc} is the cross correlation coefficient at $\Delta\tau_{obs}$. The bubble ascending speed is

$$w_b = \Delta l/\Delta\tau_{true} = \Delta l K_{cc}/\Delta\tau_{obs}, \qquad (3.74)$$

Δl being the distance between the pressure measurement points.
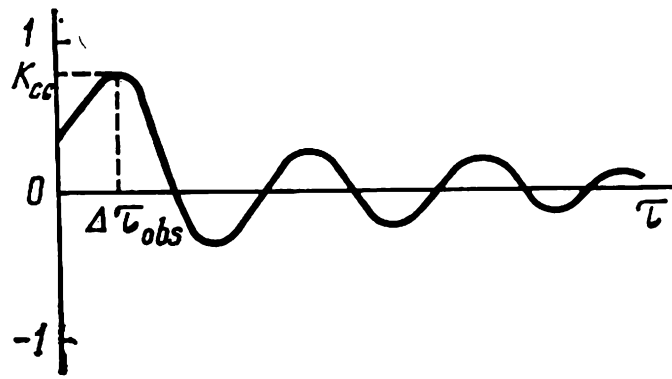
Fig. 82. Determination of time lag

The ascending speed is determined in the upper portion of the bed, where no radial displacement of the bubble is observed and its growth can be ignored. The distance Δl must be shorter than the bubble diameter to satisfy the following inequality:

$$\Delta l/w_b \leqslant 1/\omega, \qquad (3.75)$$

where ω is the fluctuation frequency.

2. DC/DA CATALYTIC REACTOR MODELS

In simulation, calculation, and optimization of the reactor performance the tendency is to use ideal hydrodynamic perfect-mixing or plug-flow models (see p. 299). In the case of reactors with a fixed (filtering) catalyst bed, a plug-flow model is often applicable under adiabatic or polythermic temperature conditions. Ideal perfect-mixing and plug-flow models are not suitable to describe catalytic processes in fluidized-bed reactors. The presence of voids (gas bubbles) in the catalyst bed as well as the mixing of the gas with solid particles complicate the chemical processes. This is taken into account in the mathematical models of such systems, known as two-phase models. What sets such models apart is the fact that the

reaction does not take place in the bubble zone, and variations in the reagent concentration are due to mass transfer involving the dense part of the bed. Currently, the so-called bubble model is widely used in the calculations associated with fluidized-bed reactors, which has been tested in the SO_2 oxidation process and has shown a good fit to the experiment under conditions when complete mixing takes place in the dense part of the bed. Consequently, this model can be recommended for calculations and optimization of fluidized-bed reactors for SO_2 oxidation at the first contact step in the DC/DA system, the catalyst beds being isothermal over the height. The calculation of the catalyst bed heights boils down to solution of the following system of equations:

$$x = \frac{K_0 \Delta x}{1 - W \exp(-Q)} ; \tag{3.76}$$

$$y = x [1 - \exp(-Q)]; \tag{3.77}$$

$$x_{\text{cat}} = Wy + (1 - W) x, \tag{3.78}$$

where x and y are the percentage conversions in the dense part of the bed and in bubbles, respectively; x_{cat} is the overall percentage conversion at the exit from the catalyst bed; $K_0 = k(T) H_0 C_0^{n-1}/w$ is the contact number; $Q = \beta H/w_b V_b$ is the phase-to-phase transfer number; $W = 1 - w_f/w$ is the amount of gas in the bubbles; C_0 is the reagent concentration; Δx is the driving force expressed in terms of percentage conversion; w_b is the ascending speed of a bubble with a surface S_b and a volume V_b; $k(T)$ is the reaction rate constant as a function of temperature; H and H_0 stand for the working and initial bed heights, respectively; w and w_f stand for the working and fluidization onset velocities, respectively; $\beta = q + \beta_0 S_b$ is the phase-to-phase flow (flow between bubbles and the dense part of the bed); q is the gas flow through a bubble; and β_0 is the coefficient of mass transfer between a bubble and the dense part of the bed.

The fluidization onset velocity w_f is determined from Eq. (3.62). The phase-to-phase transfer number Q can be calculated with respect to the equivalent bubble diameter. Substitution of the gas flow through a bubble and the rate of mass transfer across the curvilinear bubble surface into the expression of the phase-to-phase transfer number gives

$$Q = \frac{H}{w_b V_b} (0.75 w_f d_b^2 + 0.785 D^{1/2} d_b^{-1/4} g^{1/4} S_b), \tag{3.79}$$

where d_b is the bubble diameter, and D is the molecular reagent diffusion coefficient. The values of d_b and w_b are calculated using the experimental data obtained in a cold model.

The calculations associated with fixed-bed reactors are based on a plug-flow model (see p. 300), and the percentage conversion

at the exit from the ith bed is determined from the kinetic equation

$$dx/d\tau = k\Delta x. \tag{3.80}$$

In the case of an adiabatic reactor, Eq. (3.80) is complemented by the adiabatic equation

$$\Delta t = \lambda x, \tag{3.81}$$

in which λ is a factor taking into account the heating of a gas mixture of a particular composition with increasing percentage conversion per 1%, and x is the percentage conversion.

Solved for an adiabatic bed are Eqs. (3.80) and (3.81), while an isothermal bed requires solution of only Eq. (3.80). To solve Eqs. (3.76) through (3.78) and (3.80) (3.81), use is made of Eq. (2.23) which is reduced, for convenience, to

$$\frac{dx}{d\tau} = k \frac{(b-ax/2)(1-x)}{(1-ax/2)[(c+ax)0.75+(1-x)]} \times$$
$$\times \left[1 - \frac{(c+ax)^2(1-ax/2)}{a^2(1-x)^2 K_{eq}^2 (b-ax/2)} \right], \tag{3.82}$$

where a, b, and c are the concentrations of SO_2, O_2, and SO_3 at the bed inlet, respectively, and $K_{eq} = p_{SO_3}/(p_{SO_2} \cdot p_{O_2}^{0.5})$ is the equilibrium constant.

The driving force of the process is

$$\Delta x = \frac{(b-ax/2)(1-x)}{(1-ax/2)[(c+ax)0.75+(1-x)]} \times$$
$$\times \left[1 - \frac{(c-ax)^2(1-ax/2)}{a^2(1-x)^2 K_{eq}^2 (b-ax/2)} \right], \tag{3.83}$$

whereas the temperature dependence of the rate constant $k = f(T)$ at a particular catalyst activity is given by the Arrhenius equation. The contact number K_0 from Eq. (3.76) takes the following form when applied to the SO_2 oxidation process:

$$K_0 = (kH_0/wa)(T/273). \tag{3.84}$$

3. EXPERIMENTAL UNITS AND PROCEDURE
A. UNIT NO. 1 WITH COLD MODEL
OF FLUIDIZED-BED REACTOR

The unit (Fig. 83) includes a model of a fluidized-bed reactor, an air feed system, an air flow rate monitoring and control system, and a measuring circuit. Inserted into the bed are two pulse tubes for pressure measurement, connected to quick-response transducers. In this work, all instruments are associated with strain gauges whose operating principle resides in measurement of the change in the resistance of a conductor which is an arm of a bridge measuring

circuit and is under strain. Signals from two transducers are applied to the strain-gauge and matching amplifiers, after which the electric signal is fed through an analogue-to-digital converter into a computer. The signal scanning programme is controlled from the operator's panel. The programme includes scanning of the zero unbalance of the transducer before and after the experiment and the main signal. The computer modes are flashed on an annunciator.
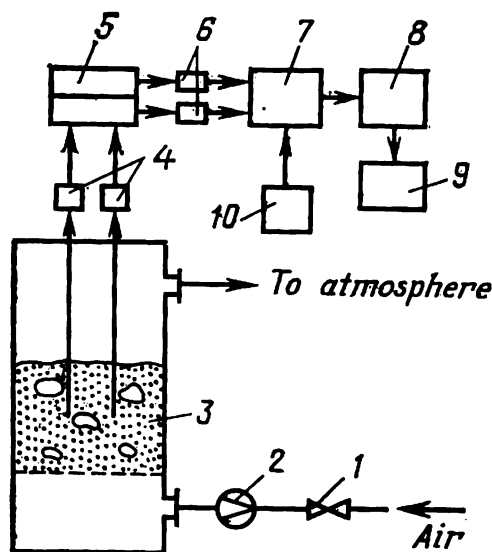
Fig. 83. Experimental setup:

1—flow controller; *2*—flow meter; *3*—fluidized-bed reactor model; *4*—pressure strain gauges; *5*—strain gauge amplifier; *6*—matching amplifier; *7*—A/D converter; *8*—computer; *9*—annunciator; *10*—remote control panel

B. UNIT NO. 2 FOR PRODUCTION OF SULPHURIC ACID IN A DC/DA PROCESS

In view of the difficulties arising in the laboratory when it comes to supplying raw materials and removing the product (particularly in sulphuric acid production), the process must be organized in such a manner as to minimize the waste and effluence with the catalytic reactors being as close in size to the industrial ones as possible. It is from these considerations that in the laboratory unit the raw material for the production of sulphur dioxide is sulphuric acid, that is the end product.

Sulphuric acid (Fig. 84) is decomposed into sulphur dioxide, oxygen, and water in the furnace *VIII*, into which it is delivered from the acid tank *X* by the pump *IX*. The gas released in the furnace flows into the drying tower *VI* refluxed with concentrated sulphuric acid and into the spray trap *VII*. The latter also serves as a receiver in which a specified positive pressure is maintained by means of a transducer *1* and an acid flow controller *2* at the entrance of the furnace. The temperature in the furnace is maintained by electric heating and controlled by a temperature transducer *3*. The dry gas in a stoichiometric ratio $SO_2 : O_2$ passes through the flow controller *4* to be mixed with air flowing through the flow controller *5*, then enters the catalytic reactor *I* of the first contact stage, with two fluidized beds. The SO_2 concentration at the reactor inlet is maintained within 8 to 15% by volume. The air flow rate is controlled by a flow trasducer *6*, while that of the SO_2 and O_2 mixture is controlled by an SO_2 concentration transducer *7*. Provided immediately upstream of the first bed in the reactor is an electric heater to maintain the required temperature in the first bed, sensed by a thermocouple *8*. The inlet gas temperature is monitored by a thermocouple *9*. Having

passed through the first bed, the gas is cooled between the beds by air coolers. The air flow into the coolers is controlled by a controller *10* through temperature which is measured by a thermocouple *11*. Another thermocouple *12* measures the temperature at the entrance of the second bed. The conversion in each bed is determined by concentration measurements at points *13* and *14*. For temperature stability, the catalyst beds are provided with external electric heating to compensate for heat losses.

From the fluidized-bed reactor the gas flows into the first-stage absorber *IV* in which SO_3 is absorbed by concentrated sulphuric acid fed from the tank *X* by the pump *IX*. Having passed through the spray trap *V*, the gas enters the second-stage catalytic reactor *II* with three fixed beds. It is heated upstream of the first bed by an electric heater up to the desired temperature controlled by a thermocouple *15*. The temperature is measured heightwise by thermocouples *16* and *17*. The temperature at the entrance of the second bed is controlled by three means: air cooler via an air flow controller *18*; blowing cold gas downstream of the first stage through a gas flow controller *19*; and blowing cold air through an air flow controller *20*. The temperature is controlled by a thermocouple *21*. Thermocouples *22* and *23* measure temperatures over the bed height. The temperature at the entrance to the third bed is controlled by an air cooler via a controller *24* and monitored by a thermocouple *25*. Thermocouples *26* and *27* are intended for measuring temperatures over the bed height. The conversion in each bed is determined from the SO_2 concentrations measured at points *28* through *31*. The gas from the fixed-bed reactor enters the second-stage absorber *III* and is vented into the atmosphere. The absorber is refluxed with concentrated acid. The rates of acid flow into the absorbers and drying tower are maintained constant under all operating conditions of the unit by valves *31* through *33*. The acid flows into the receiver by gravity. The acid in the receiver is cooled by a water cooler where water is fed through a valve *34*. If necessary, the acid in the receiver can be diluted to the desired concentration through a valve *35*. During operation, the gas collector communicates with the first-stage absorber (to reduce the hydraulic seal height), and when the unit is shut down, it can be made to communicate with the atmosphere via a valve *36*. The pump is disconnected from the system for repair by valves *31* through *33*, *37*, and *38*. The acid is delivered for neutralization via a valve *39*. The same valve can be used to sample the acid for analysis. The acid level is monitored by the level transducer *40*.

Since the SO_2 conversion at both stages is 99.0 to 99.8%, a certain amount of sulphur dioxide is inevitably lost. To compensate for the loss, provision is made for continuous or periodic replenishment of SO_2 from a bottle. The associated monitoring and control involve a valve *41*, a controller *42*, and a flow meter *43*. The catalyst in
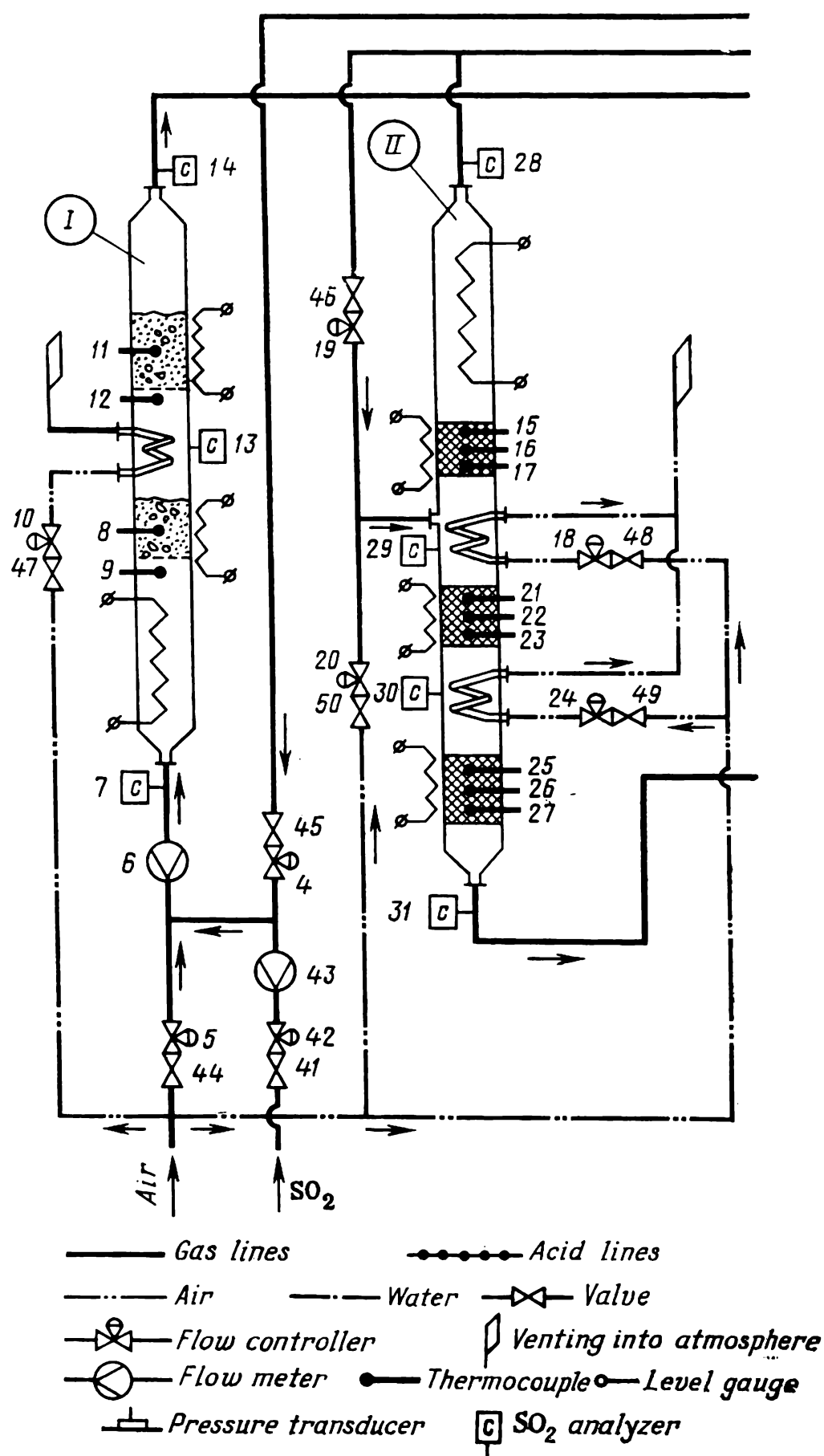
Fig. 84. Sulphuric acid unit

Gas lines ———— ●●●●●● Acid lines

——···—— Air ——··—— Water ——▷◁—— Valve

Flow controller Venting into atmosphere

Flow meter ●—— Thermocouple ○—— Level gauge

Pressure transducer [c] SO₂ analyzer
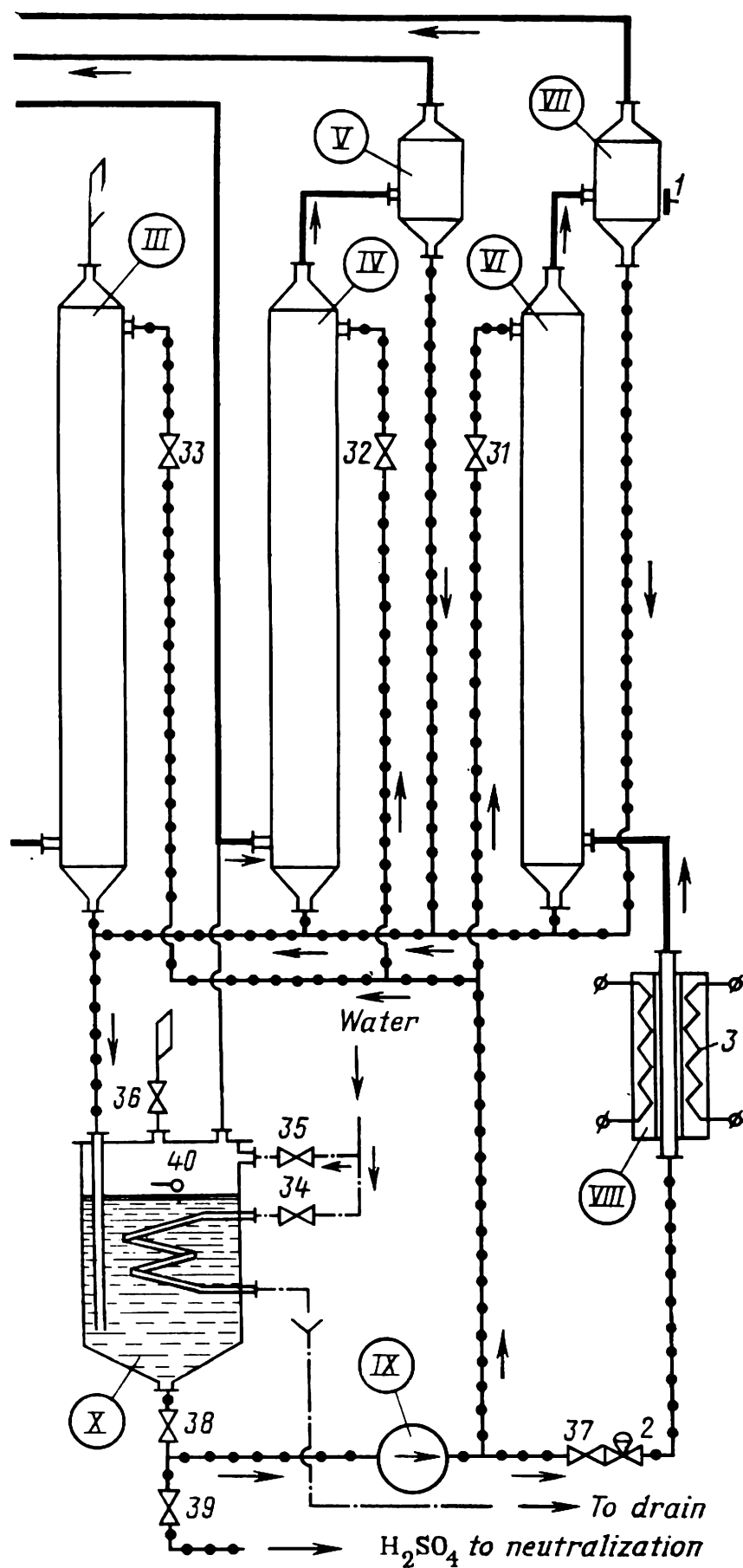
both reactors is heated and blown with air through a valve *44*, the gas lines being shut off by valves *45* and *46*, the air lines, by valves *47* through *50*, and all the electric heaters of both reactors being switched on. The basic process variables are as follows: furnace temperature—800 to 850°C; fluidized-bed temperatures—480 to 620°C; temperatures at the exits from the fixed beds—410 to 500°C; gas velocities during operation over the entire cross-section—0.3 to 0.7 m/s; SO$_2$ concentrations at the inlet of the fluidized-bed reactor—8 to 15% by volume; and catalyst grain size in the fluidized-bed reactor—0.3 to 1.5 mm. The fluidized-bed reactor is charged with a wear-resistant vanadium catalyst, while the fixed-bed reactor may use any commercial vanadium catalyst. The material balances are tied to the actual sizes of the catalytic reactors and absorbers.

PROBLEM 1. EXPERIMENTAL DETERMINATION OF PARAMETERS OF THE FLUIDIZED-BED REACTOR MODEL

The experiment is carried out on unit No. 1 (see Fig. 83). It is necessary to determine the mean bubble size across the bed and the bubble ascending speed at specified bed height H_0, mean particle size d, difference Δw between the working velocity w and fluidization onset velocity w_f, height h of a measurement plane in the bed above the gas-distributing grid, and distance Δl between the measurement planes.

Before the experiment, the programme whose flow chart is shown in Fig. 85 is put in the computer. When the programme is initiated from punch cards, additional data are entered, then the control is transferred to the remote control panel (RCP) of the unit. The transducers are polled, and appropriate programme messages follow. If an error is detected in the input data, the programme can be reset by bringing the RCP to position "1". After polling, the zero levels of amplifier unbalance before (A_{0i}) and after (A_{0f}) the experiment are compared. If the difference exceeds the preset value ε, the programme is reset. The mean values, mean relative deviations for axial and radial pressure fluctuations, as well as the cross correlation functions are calculated at permissible deviations. To determine the bubble size, one must calculate the mean absolute deviations for axial and radial fluctuations in real units[1]

$$\overline{\Delta\Delta P} = \psi\overline{\Delta P}_\text{bed.} \qquad (3.85)$$

where $\overline{\Delta P}_\text{bed}$ is the mean bed resistance measured by a U-tube gauge. Then, the coefficient K (Fig. 80) is determined from the ratio between the mean values of axial and radial fluctuations. The mean

bubble radius is defined by substituting K and $\overline{\Delta\Delta P}$ into Eq. (3.71) or (3.72).

The calculation of the bubble ascending speed boils down to substitution of the time lag $\Delta\tau_{obs}$ and cross correlation coefficient
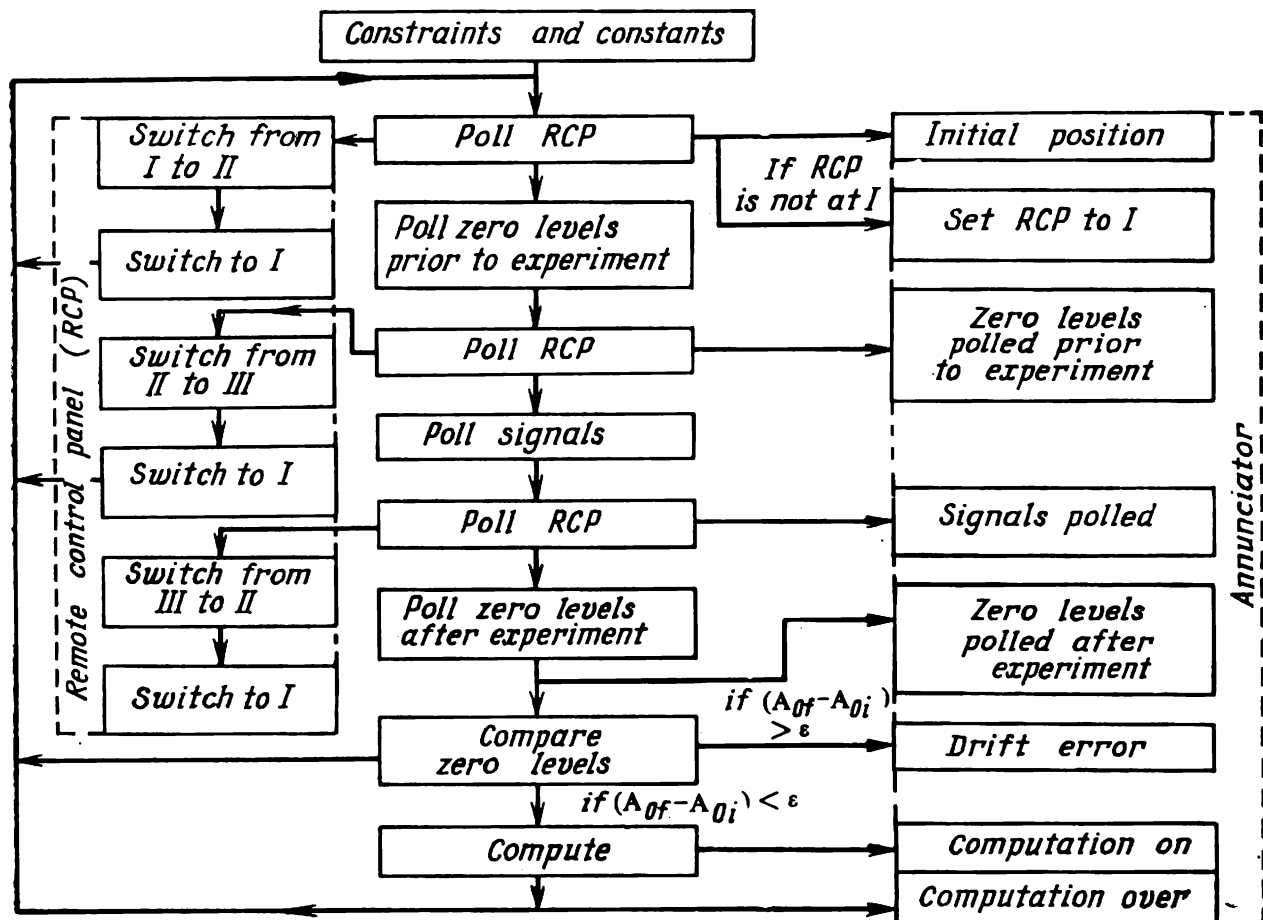
Fig. 85. Block diagram of the programme

K_{cc}, taken from the plot of the cross correlation function (see Fig. 82), into Eq. (3.74). The calculation results are presented in the form of plots (see Fig. 81 and 82) and the following table

Variant No.	Assignment			Mean bed resistance $\overline{\Delta P}_{bed}$	Relative deviation		Mean absolute deviation				Bubble radius r_b	Lag $\Delta\tau_{obs}$	Cross correlation coefficient, K_{cc}	Bubble ascending speed w_b
	Δw	Measurement plane height, h	Distance between measurement planes Δl		ψ_{ax}	ψ_{rad}	$\overline{\Delta\Delta P}_{ax}$	$\overline{\Delta\Delta P}_{rad}$	$\dfrac{\overline{\Delta\Delta P}_{ax}}{\overline{\Delta\Delta P}_{rad}}$	K				

PROBLEM 2. ANALYSIS OF OPTIMAL TEMPERATURE CONDITIONS IN THE FLUIDIZED- AND FIXED-BED REACTORS OF A DC/DA CONTACT UNIT BASED ON MATHEMATICAL MODELS

At specified gas flow rate, SO_2 concentration at the fluidized-bed reactor inlet, and catalyst bed heights at the first and second contact stages, analysis is made to derive the maximal overall conversion of SO_2 to SO_3 at both contact stages, using mathematical models of the reactors. The problem is reduced to selection of optimal temperatures for each catalyst bed.

The systems of equations (3.76) through (3.78) plus Eqs. (3.80) and (3.81) are used to calculate, at specified initial parameters, for each catalyst bed in both reactors the relation $x = f(t)$ in the temperature range from the ignition point $t_{ign} = 400°C$ to the levels at which the percentage conversion x will pass through a maximum. Such a curve is shown in Fig. 86. The equilibrium curve is calculated using Eq. (2.21). The calculation for the fixed-bed reactor is carried out under two condition: (1) all beds are adiabatic and (2) all beds are isothermal. The resulting optimal temperatures are compared with the values derived from Eq. (2.24). When temperatures are determined for conditions under which the gas is fed into the space below the second bed of the fixed-bed reactor through a by-pass line or air is blown through the bed, the percentage conversion upstream of the second bed is determined from the equation

Fig. 86. $x = f(t)$
1—equlibrium curve; *2*—calculated curve

$$x_{bed\ 2} = 1 - (1 - x_{bed\ 1})\frac{V_1}{V} + \frac{V_2}{V}, \qquad (3.86)$$

in which $x_{bed\ 1}$ is the conversion downstream of the first bed of the fixed-bed reactor; V_1 is the volume of the gas passing through the fixed-bed reactor per unit time; V_2 is the additional gas volume applied upstream of the second bed per unit time; and $V = V_1 + V_2$.

The calculations are made with the aid of a computer. The software is oriented to a particular computer. The calculation results are tabulated as follows:

Reactor	Bed number	H_0	Gas flow rate	t_{opt} in accordance with mathematical models	t_{opt} in accordance with Eq. (2.24)	Conclusions
Fluidized-bed	1 2					
Fixed-bed	1 2 3					

PROBLEM 3. EXPERIMENTAL VERIFICATION OF THE RESULTS OF OPTIMIZATION ANALYSIS OF THE CONTACT UNIT PERFORMANCE

The experiment is conducted on unit No. 2 (see Fig. 84). The results are used to establish respective temperature conditions in the fluidized- and fixed-bed reactors at specified initial parameters, and the agreement between the calculated and experimental percentage conversions in each bed and at the reactor outlet is checked. To this end, the contact plant (Fig. 84) must be heated to the starting temperatures at which the system is normally blown with air, and the furnace *VIII* must be heated to the working temperatures. For this purpose, acid is delivered to reflux the drying tower *VI* and absorbers *IV* and *III* via the valves *31* through *33* with the valve *38* open and the pump *IX* switched on. All electric heaters of both reactors and the furnace are energized. Air is fed via the valve *44* with the valves *41* and *45* through *50* closed. Next, cooling water is fed into the cooler of the acid tank *X* via the valve *34*. The valves *35*, *36*, and *39* are closed. The air flow rate is adjusted by the flow meter *6* so that the air velocity in the fluidized-bed reactor exceeds the fluidization onset velocity by 0.1 to 0.2 m/s, calculated at bed temperatures. The rate of acid feed into the furnace via the valve *37* is set to a minimum by the controller *2*, to provide for positive gas pressure in the receiver *VII*, necessary for operation of the unit.

For the ignition point (410-440°C), measured by the thermocouples *8*, *11*, *15*, *21*, and *25*, to be attained in all beds of the contact unit, the gas flow rate and SO_2 concentration at the entrance of the first bed, specified in the assignment, are preset. To this end, the valve *45* is slowly opened, and automatic control of the flow rate and concentration at the inlet of the fluidized-bed reactor by the controllers *4* and 5 is initiated.

The calculated temperatures in the beds are attained with the aid of electric heaters and air coolers by opening the valves *47* through

49 and initiating automatic flow rate control by the controllers *10*, *18*, and *24*. In the case of air being blown upstream of the second bed, the valve *46* or *50* is opened, and the rate of gas or air flow through the bypass is adjusted by the controller *19* or *20*, respectively. The SO_2 concentrations downstream of each bed are measured, and the percentage conversion in each bed is calculated. In the fluidized-bed reactor, the temperature is varied in the first then in the second bed within $\pm 30°C$ of the optimum.

After the experiment, the catalyst beds are purged of SO_3 with air at temperatures in the neighbourhood of 500°C for two to three hours. The sequence of valve actuation is reverse, as compared to that during heating of the beds. The furnace is switched off before the beds are purged. After the purging is over, the electric heaters of the fluidized- and fixed-bed reactors are de-energized, and all valves are closed.

The experimental results are tabulated as follows:

Reactor	Bed number	t_{opt} in accordance with analysis, °C	t_{opt} in accordance with Eq. (2.24)	Experimental t_{opt}	Conclusions
Fluidized-bed	1 2				
Fixed-bed	1 2 3				

Conclusions are drawn as to applicability of the mathematical models in practical calculations.

LITERATURE

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Chemical Technology, Mukhlyonov, I. P., Averbukh, A. Ya, Tumarkina, E. S. *et al.*, 3rd revised and expanded edition, Moscow, 1977, part II, pp. 7-31.

Himmelblau, D., *Process Analysis by Statistical Methods*, Moscow, 1973, p. 957.

Instructions to the Laboratory Work "Optimization of a Contact Unit of Sulphuric Acid, Operating on a Double Contact-Double Absorption Principle"

1. Authorization to operate this unit is given to students duly instructed at the working station in the safety precautions to be taken while handling noxious substances, electric devices and appliances, as well as in first aid procedures.

2. The laboratory unit must be installed under an exhaust hood. The electric heaters of the reactor and electric measuring instruments are energized from 220 V mains. The protective gear must include acrylic plastic goggles or masks, rubber gloves and apron, to be used when handling concentrated sulphuric acid, as well as a gas mask of the B or C type (blue canister) for possible contamination of the room with sulphur dioxide (MPC 10 mg/m^3). All electric cables from the reactor must be properly insulated and the measuring instruments zeroized.

3. Perform the experiment in compliance with the unit startup and operation manual. In case of emergency close the bottle with sulphur dioxide and shut down the acid evaporator to avoid contamination of the room. Switch off the air blower and all electric instruments and heaters.

LABORATORY WORK 24. ANALYSIS OF HETEROGENEOUS CATALYTIC PROCESSES ON AN AUTOMATED CONTINUOUS-CIRCULATION UNIT

The processes occurring in heterogeneous catalysis over porous catalysts involve transfer of the gas (or liquid) phase onto the catalyst grain surface and diffusion of the reagents inside the porous structure. The heat transfer follows a similar pattern.

The kinetics of catalytic reactions is studied by two methods—continuous and continuous-circulation. The continuous method permits conducting a reaction under stationary conditions. However, it is assumed that the gas moves through the catalyst bed in a plug-flow pattern. This assumption holds but approximately only at a low gas flow rate and with the catalyst bed height exceeding the grain size considerably. Therefore, when comparison is made with experimental data, the kinetic equation must be integrated with respect to the contact time, volume or height of the catalyst bed. The continuous method is convenient and widely applied in routine testing of catalysts, preliminary evaluation of their activity, and deriving the kinetic characteristics under similar conditions when comparative rather than absolute values are more important.

The difficulties associated with the continuous method also arise as a result of concentration and temperature gradients in the reaction zone. These difficulties are obviated by using gradient-free methods. The gradient-free principle was for the first time realized by M. I. Temkin, S. L. Kiperman, and L. I. Lukyanova in a continuous-circulation method. It permits circulating a gas mixture in a closed loop with the catalyst, with simultaneous injection of the starting gases and removal of the product mixture. In this case, the rate of injection and removal of the gas mixture must be low in comparison with the circulation rate to ensure insignificant conversion of the components per pass over the catalyst, which eliminates the concentration and temperature gradients. As a result of the

high circulation rate and, consequently, intensive mass and heat transfer, the process is characterized by plug-flow conditions with an isothermal catalyst bed. Therewith, any combination of the contact time and linear gas velocity is possible. By varying the flow rate, one can gain an insight into the conversion over different cross-sections of the catalyst beds in an industrial reactor.

The reaction rate u can be determined directly from the amount of the product formed per unit reaction volume (or catalyst amount) per unit time, which is why no integration of the kinetic equations is necessary, whereby analysis of the experimental data is significantly simplified:

$$u = V_g \frac{C_{pr.f} - C_{pr.i}}{v} = \frac{C_{pr.f} - C_{pr.i}}{\tau}, \qquad (3.87)$$

where V_g is the gas mixture flow rate, in m³/h; $C_{pr.f}$ is the final product concentration in the gas mixture, in % by volume; $C_{pr.i}$ is the initial product concentration in the gas mixture, in % by volume; v is the bulk volume of the catalyst, in m³; and $\tau = v/V_g$ is the time of contact between the gas and catalyst (theoretical), in h.

The above advantages of the continuous-circulation method attest to its applicability in analysis of the kinetics of such catalytic processes as synthesis and oxidation of methanol, ammonia synthesis, oxidation of sulphur dioxide, and others.

This work deals with the kinetics and mechanism of catalytic conversion of methanol to formaldehyde over an iron-molybdenum oxide catalyst in a filter bed at different process variables*.

In the industrial process, formaldehyde is produced over a silver-on-pumice catalyst. Here, the methanol content in the product ranges from 5 to 10%. When an iron-molybdenum catalyst (Fe_2O_3 19%, MoO_3 81%) is used, the conversion of methanol may yield formaldehyde free of methanol, in accordance with the reaction

$$CH_3OH + 1/2O_2 = CH_2O + H_2O$$
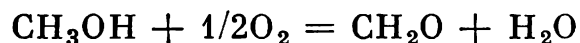
The process can be studied using an ordinary non-automated continuous-circulation unit. Of particular interest, however, is an automated unit with computer-aided control and optimization of the process.

Non-Automated Unit and Experimental Procedure

The continuous-circulation unit for heterogeneous catalytic conversion of methanol is shown schematically in Fig. 87. The unit has a complex arrangement with a great number of interrelated variables.

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* The same unit can be used in studying other catalytic processes as well.

It can be divided into the following four basic systems: (1) metering and purification of oxygen and nitrogen; (2) metering of methanol; (3) circulation loop (electromagnetic positive displacement pump, valve box, reactor); and (4) absorption system.

50 to 70 cm^3 of methanol are heated in the alcohol evaporator *8* to 20-40°C (with a high degree of accuracy) with the aid of a thermostat *10*. Nitrogen is fed from the bottle *1* through fine-control valves *2*
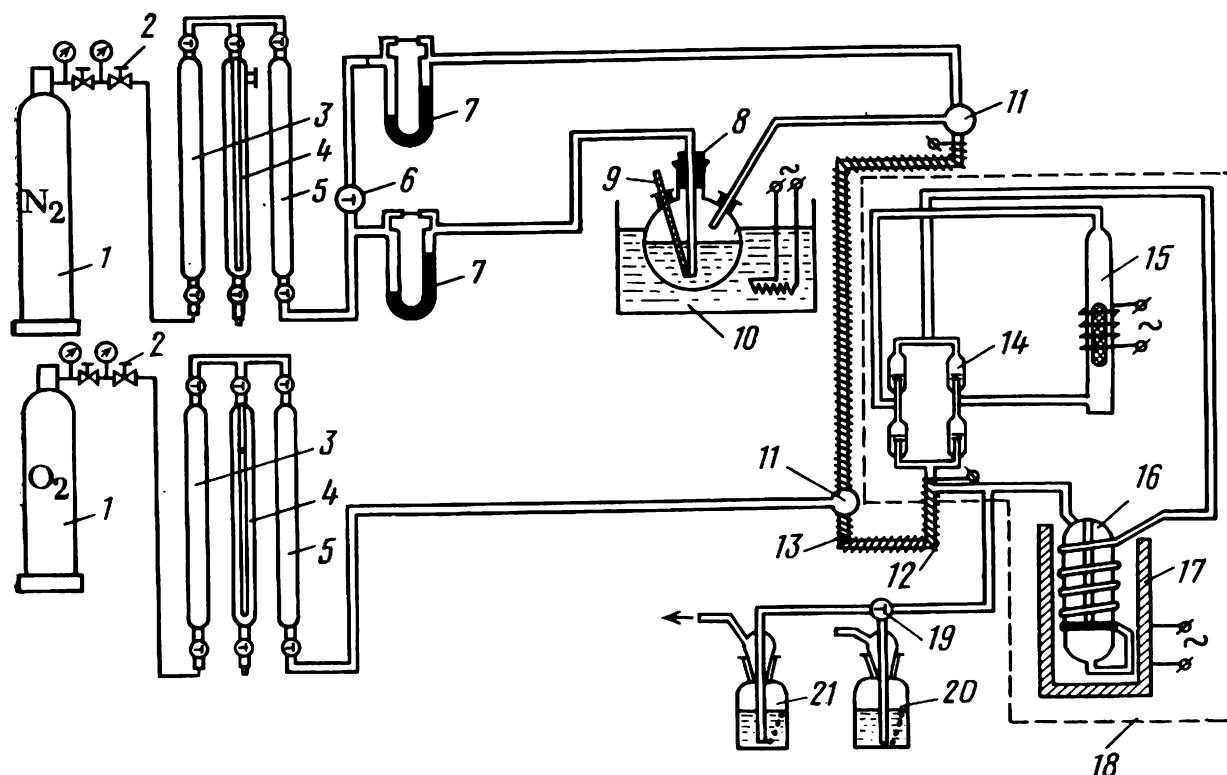
Fig. 87. Continuous-circulation unit for heterogeneous catalytic conversion of methanol to formaldehyde

1—bottle; *2*—fine-control valve; *3*—gas scrubber; *4*—manostat; *5*—drying column; *6,19*—cocks; *7*—rheometer; *8*—alcohol evaporator; *9*—thermometer; *10*—thermostat; *11*—mixer; *12*—superheater; *13*—flame trap; *14*—valve box; *15*—positive displacement pump; *16*—reactor; *17*—furnace; *18*—air thermostat; *20, 21*—Drexel bottles with water

and manostat *4* at a rate of 3 to 9.5 dm^3/h and passes through methanol in the alcohol evaporator *8*. The resulting nitrogen-alcohol mixture flows through the superheater *12* and, after having been mixed with oxygen in the mixer *11*, enters the circulation loop via a flame trap *13*. The temperature in the reactor *16* of the circulation loop is maintained constant within 280 to 340°C. Here, the oxygen-alcohol mixture passes through the bed of an iron-molybdenum oxide catalyst, arranged between two quartz beds, to promote the conversion of methanol at a given temperature.

The condensed reaction products (formaldehyde as well as the unreacted methanol and reaction water) are absorbed by water in the Drexel bottle *21*. After the process has steadied itself, all of the gas is let by the cock *19* through the Drexel bottle *20* with water over a predetermined time interval. The resulting solution is sampled

from the Drexel bottle *20* and analyzed for formaldehyde and methanol contents (see Work 19). For subsequent determination of the reaction rate with respect to the reacted methanol, the volume concentrations at the reactor inlet and outlet must be calculated using the equations

$$C_{m.1} = \frac{V_n}{V_g} \left(\frac{1}{P_0 P_t - 1} \right) \cdot 100 , \qquad (3.88)$$

$$C_m = \frac{v_w 22.4 \cdot 100}{\tau M_m (100/C'_m - 1) V_g} , \qquad (3.89)$$

where $C_{m.1}$ is the concentration of methanol downstream of the evaporator and upstream of the reactor, in % by volume; C_m is the methanol concentration at the outlet after the conversion cycle, in % by volume; V_n is the rate of nitrogen flow through the evaporator, in m³/h; V_g is the overall gas mixture flow rate, in m³/h; P_0 is the atmospheric pressure; P_t is the pressure of saturated methanol vapours in the evaporator at temperature t; C'_m is the methanol concentration in the absorption bottle (based on chemical analysis), in % by weight; M_m is the molecular weight of methanol; τ is the time of sampling into the Drexel bottle; in h; and v_w is the volume of water in the Drexel bottle, in cm³.

Here is an example of calculation of the reaction rate using Eq. (3.87): if $V_g = 10$ dm³/h $= 0.01$ m³/h; $v_w = 3$ cm³ $= 3 \cdot 10^{-6}$ m³; $C_{m.1} = 5\%$ by volume; and $C_m = 2\%$ by volume, then

$$u = \frac{0.01 (5 - 2)}{3 \cdot 10^{-6}} = \frac{0.01 \cdot 3}{3 \cdot 10^{-6}} = 30\,000 \text{ h}^{-1}.$$

Automated and Computerized Continuous-Circulation Unit

Optimization of the catalytic methanol conversion process at a continuous-circulation unit and determination of the reaction rate constants within a definite temperature range call for a series of experiments with the unit operating in the search mode. This task can be accomplished with the aid of a computer and by initiating automatic control.

The layout of the automated unit remains the same with the exception of rheometers that are replaced by automatic gas flow transducers. For simplicity, the diagram of Fig. 87 is represented in Fig. 88 by individual items. The unit now incorporates some new components: a chromatograph, an automatic control system (flow, concentration and temperature transducers, measuring and control devices, actuators), and a computer.

To optimize the process one must know some decisive variables and their combinations. Such variables include the contact time, reagent and reaction product concentrations, and temperature in the reaction zone. The automated unit for conversion of methanol

to formaldehyde is structurally analogous to the other units described above (see Fig. 64). Automation provides for a system of acquisition and reduction of process data received from the transducers of the continuous-circulation unit. The computer software polls the transducers, and the polling results underlie the necessary process computations, the reduced data being presented in any convenient form (tables, plots, etc.).
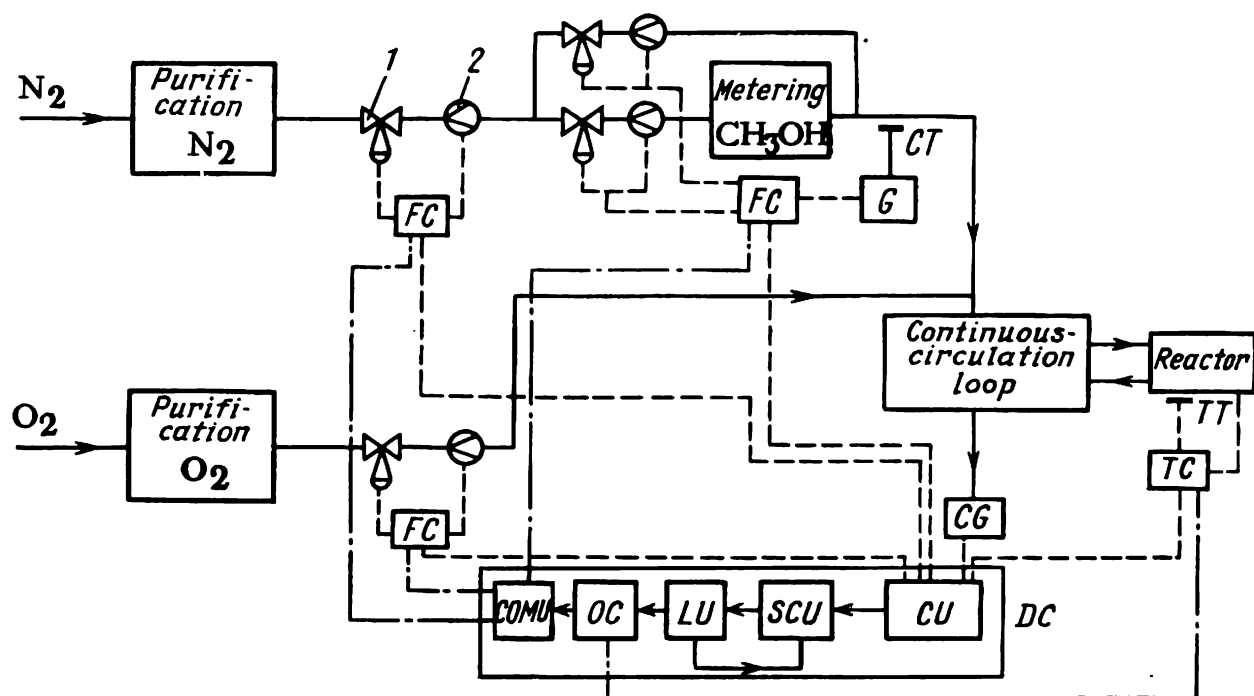
Fig. 88. Automated unit for conversion of methanol to formaldehyde:

1—flow control valve; *2*—gas flow transducer; *FC*—flow controller; *CT*—concentration transducer; *G*—gas analyzer for determining the methanol concentration in nitrogen; *TT*—temperature transducer; *TC*—temperature controller; *CG*—chromatograph ЛХМ-7а; *DC*—digital computer; *CU*—computer unit; *SCU*—storage and comparison unit; *LU*—logic unit; *OC*—optimization controller; *COMU*—comparison unit; — — — —from controlled unit to computer; —.—.— —from computer to controlled unit

The second part of this work resides in optimization of the reactor performance with the aid of the computer, based on a mathematical model of the process, using the selected optimization criterion.

The mathematical model of the catalytic formaldehyde production process in the reactor under consideration with an isothermal catalyst bed is given by

$$u = V_g \frac{C_{m.1} - C_m}{v} = k \frac{C_m^{0.5}}{\left[1 + 0.5 \frac{C_{form}}{C_m - C_{ox}^{0.5}}\right]^{0.5}}, \qquad (3.90)$$

$$v_r \frac{dC_m}{d\tau} = V_{g.1} C_{m.1} - V_{g.f} C_m \frac{T}{T_0} - v_r u, \qquad (3.91)$$

$$v_r \frac{dC_{ox}}{d\tau} = V_{g.1} C_{ox.1} - V_{g.f} C_{ox} \frac{T}{T_0} - 0.5 v_r u, \qquad (3.92)$$

$$v_r \frac{dC_{form}}{d\tau} = v_r u - V_{g.f} \cdot \frac{T}{T_0}, \qquad (3.93)$$

plus the equation of the overall gas mixture flow rate

$$V_{g.f.} = V_{g.i.} + 0.5v_r u, \qquad (3.94)$$

where C_m, C_{ox}, and C_{form} stand for the concentrations of methanol, oxygen, and formaldehyde, respectively, in the gas mixture, in % by volume; $C_{m.i.}$ and $C_{ox.i.}$ are the initial concentrations of methanol and oxygen, respectively, in the gas mixture at the inlet of the plant, in % by volume; k is the reaction rate constant, in h^{-1}; v_r is the reactor volume, in m^3; $V_{g.i.}$ and $V_{g.f.}$ stand for the gas mixture flow rates at the plant inlet and outlet, respectively, in m^3/h; T is the temperature in the reactor, in K; and u is the reaction rate with respect to the oxidized methanol, in h^{-1}.

Optimization of the reactor performance resides in search for the optimal contact temperature t and optimal methanol to oxygen ratio $(C_{CH_3OH} : C_{O_2})$ for a given percentage conversion. The results of analysis for component concentrations are transmitted from the chromatograph directly to the computer. The latter decodes the message and, having received the parameter representing the formaldehyde yield, enters the data in the storage and comparison unit.

The automatic variation of the methanol to oxygen ratio is rendered difficult by the fact that the atmospheric oxygen is in the gas phase, while methanol is in the liquid phase. In the experimental plant, methanol is metered with the aid of the alcohol evaporator. The methanol metering rate and, consequently, its concentration in the initial mixture can be varied by manipulating the control signal from the ratio unit of the flow regulators of the nitrogen passed through the alcohol evaporator or bypassing the latter.

The temperature in the reactor must be maintained constant to within $\pm 0.1°$. This is done by adding to the main heating coil of the furnace a supplementary control coil in which the current is varied in accordance with the signal from the automatic two-position potentiometer (whose sensor is a thermocouple). The value of the constant temperature maintained by the potentiometer may vary depending on the signal from the optimization unit of the computer. Besides, the reaction rate constant can be calculated using Eqs. (3.90) through (3.94).

Thus, the following tasks can be accomplished at the experimental plant:

1. Determination of the rate constant for a given catalyst at constant temperature and other process variables.

2. Calculation of the activation energy from the rate constants at various temperatures.

3. Refinement of the exponent in the kinetic equation (3.90) in the case of varying catalyst activity.

4. Definition of the optimal values of the process variables taken in various combinations.

LITERATURE

Ioffe, I. I. and Pismen, L. M., *The Engineering Chemistry of Heterogeneous Catalysis*, Moscow-Leningrad, 1972.
Franks, R., *Mathematical Modelling in Chemical Technology*, Moscow, 1971.

Instructions to the Laboratory Work "Analysis of Heterogeneous Catalytic Processes on an Automated Continuous-Circulation Unit"

1. Adjust the total nitrogen and oxygen flow rates with the aid of the valve.
2. Energize the heating coils of the alcohol evaporator, superheater, and air thermostat of the circulation cycle.
3. Switch on the positive displacement pump.
4. Switch on the reactor heating.
5. As soon as the specified temperature is attained in the alcohol evaporator, adjust the rates of nitrogen flow through the alcohol evaporator and bypass lines in accordance with the selected methanol concentration.
6. De-activate the system in the following sequence: switch off all heaters, cut off the nitrogen supply into the alcohol evaporator, and, when the reactor is cooled, switch off the positive displacement pump and cut off the nitrogen and oxygen supplies.
7. Take all the necessary precautions in handling inflammable and toxic liquids (see instructions).
8. Take all the necessary precautions in handling electric heaters and other appliances (see instructions).
9. Take the readings of the instruments indicating the methanol concentration in the gas mixture upstream of the circulation loop to avoid formation of an explosive mixture. In case of emergency, manually cut off the supply of nitrogen into the alcohol evaporator and call the instructor.

LABORATORY WORK 25. ANALYSIS OF REACTOR MODELS

In reactor studies wide use is made of process simulation and calculation of the necessary variables, based on the derived model. Hence, this work deals with investigation of chemical conversion in various types of reactors and comparative analysis of reactor models for selection of the best. The number of parts in this work corresponds to that of reactor models. The first part is concerned with chemical reactions in a continuous tubular reactor, the second deals with a batch perfectly mixed reactor, and the third part covers chemical reactions in a continuous perfectly mixed reactor and in a cascade of such reactors.

A. CONTINUOUS TUBULAR REACTOR

The material balance (mathematical model of the reactor) of plug flow under steady-state conditions is written as

$$w \frac{dC_A}{dH} = u_A, \qquad (3.95)$$

where C_A is the concentration of the main starting component A, in mole/dm³; w is the linear velocity of the flow, in m/s; H is the reactor height (length), in m; and u_A is the reaction rate, in mole/(m³·s)

Calculations of a plug-flow reactor are based on an equation derived from the material balance of the reactor:

$$\tau = C_{A0} \int_0^{x_A} \frac{dx_A}{u_A}, \qquad (3.96)$$

where τ is the residence time of the main reagent A; C_{A_0} is the initial concentration of the component A, in mole/dm³; and x_A is the percentage conversion.

Continuous tubular reactors with a length-to-diameter ratio exceeding 10 operate under conditions close to plug flow.

In a real reactor, reverse axial and radial mixing may take place. The diffusion model of a tubular reactor, taking into account axial (longitudinal) mixing, takes the form

$$w \frac{\partial C_A}{\partial H} = u_A - D \frac{\partial^2 C_A}{\partial H^2}. \qquad (3.97)$$

The departure of the reaction mass flow in a real reactor from that in an ideal one depends on the longitudinal mixing coefficient D, flow velocity w, and the reactor length. This departure can be determined by comparing the volumes of the ideal and real reactors (or residence time in both) to provide for the same conversion of the reagent.

In this work, a plug-flow reactor is analyzed using the following second-order equation, representing saponification as ethyl acetate with an alkali, as an example:
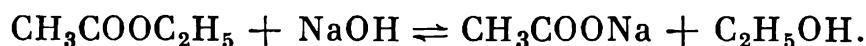
$$CH_3COOC_2H_5 + NaOH \rightleftharpoons CH_3COONa + C_2H_5OH.$$

The work includes: (1) studying the effect of the reactor hydrodynamics on the process variables; (2) application of kinetic laws in the modelling, selection, and calculation of the reactors; (3) computer simulation of the process and computation of its variables for different conditions, using an ideal model; (4) comparison of the data from a real reactor with those computed for the ideal model, as well as determination of the departure from the ideal and the effect of the process conditions on the extent of the departure; and (5) comparison and analysis of the data obtained when the same reaction is conducted in plug-flow, batch and continuous completely mixed reactors, based on material balances.

Experimental Setup and Procedure

The starting reagents are fed into the reactor *17* (Fig. 89) from thermostats *8* (0.1 *M* NAOH) and *9* (0.1 *M* ethyl acetate). A constant liquid level is maintained in the thermostats with the aid of controllers. Contact thermometers *15* and *16* are proved to preset and control the temperature in the thermostats *8* and *9*. The reagents flow into the reactor by gravity. The reagent feed rate is controlled by valves *11* and *13* and measured by rotameters *10* and *12*.

The reagents are fed at a preset rate into the plug-flow reactor *17* which is in the form of a tube 8 mm in diameter. The reagents are let into the reactor by cocks *14*. To maintain a constant temperature in the reactor, it is placed in a thermostat *18*, through which a heat-transfer agent circulates at a particular temperature.

The reagents—NaOH and ethyl acetate solutions—react as they pass through the reactor. The NaOH concentration over the reactor length is measured by cells *2* through *6* provided with cocks. It is

Fig. 89. Plug-flow reactor

determined from changes in the conductivity of the mixture. The conductivity is measured with the aid of an automatic bridge *7* of the KCM-4 type, which permits the process to be monitored continuously without taking samples.

The experiment is conducted in the following sequence. The starting reagents, NaOH and ethyl acetate solutions, are poured into the thermostats *8* and *9* with the valves *11* and *13* closed. The thermostats *8* and *9* are switched on, and the desired temperature is preset with the aid of the contact thermometers *15* and *16*. The same temperature is preset in the thermostat *18*. The cocks of the cells *2* through *5* are closed, while the cock *14* and that of the cell *6* are opened. The valve *11* adjusts the NaOH solution flow rate with reference to the rotameter *10*, and the valve *13* does the same with the ethyl alcohol solution rate with reference to the rotameter *12*. After the temperature in the system has reached the specified level, the resistance in the last cell *6* is measured. The measurement is repeated several times after two to three minutes before a stable resistance read-

ing is taken, which is indicative of the reactor having attained steady-state conditions. Then, the resistance is measured in the next cell. To do this, first the cock on the cell *5* is opened and only then that on the cell *6* is closed, and not the other way round so as not to disturb the flow pattern in the reactor. Resistance measurements are taken in all cells. In each cell, the measurement is repeated two or three times. The alternation of cells in the course of measurement may be in any sequence.
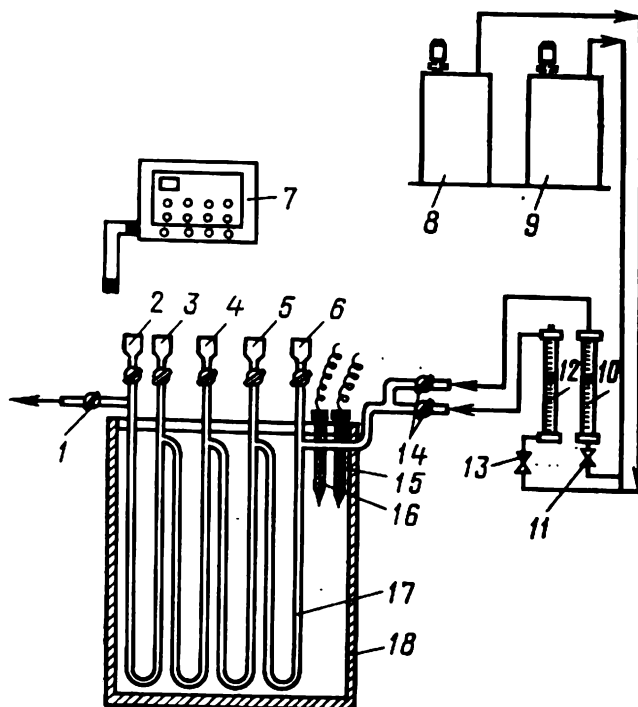
The initial alkali and ethyl acetate concentrations at the reactor inlet are calculated from the reagent concentrations in the starting solutions and the ratio of their flow rates.

The reactor volume is calculated using the formula

$$v = \frac{0.785 d^2 l}{1000},$$ (3.98)

where d is the internal diameter of the reactor tube, equal to 0.8 cm, and l is the reactor tube length.

The residence time of the reagents is determined from the formula

$$\tau = v/V,$$ (3.99)

where v is the reactor volume, in dm^3, and V is the reagent flow in dm^3/h.

The NaOH concentration is determined from the calibration resistance-versus-concentration curves. The ethyl acetate concentration is calculated with due account for its initial content and its amount entering into the reaction. The latter is equivalent to the amount of the reacted NaOH, which can be determined by comparing the initial and current NaOH concentrations. The reagent conversion x_A is found from the formula

$$x_A = (C_{A_0} - C_A)/C_{A_0}.$$ (3.100)

This work involves one of the following assignments: studying the dependence of variations in the basic process variables, such as concentration and conversion of NaOH and ethyl acetate over the reactor length, on different operating conditions; determination of the effect of the reagent feed rate, the ratio between the flow rates of NaOH and ethyl acetate (i.e., initial NaOH and ethyl acetate concentrations), and temperature on the process variables; and plotting of curves on the basis of the available data.

The reagent flow rates may equal 3, 4, 5, 6, or 7 l/h; the ratio between the flow rates of the alkali and ethyl acetate may be 1 : 2, 1 : 3, 1: 4, or 1 : 5; and the temperature may be equal to 20, 25, 30, 35, or 40 °C. The concentration of the reagents in the initial solutions (in the tanks) may be as follows: NaOH—0.1 mole/l, and ethyl acetate—0.1 mole/l.

The ethyl acetate saponification process in a plug-flow reactor is simulated in this case. The mathematical model of the process includes Eq. (3.96) for an ideal reactor and the kinetic equation

$$-u_A = kC_{NaOH}C_{ea}. \qquad (3.101)$$

(In the case of significant dilution, the ethyl acetate saponification reaction may be considered as practically irreversible.) The value of the rate constant k is either derived when the experiment involves a batch reactor or taken from the literature.

The extent of departure from the ideal at a particular percentage conversion x_A is defined by comparing the time τ of residence of the reagents in the real reactor, calculated from the experimental data, with the time τ_{1d} of residence in the ideal reactor, calculated theoretically on the model with the aid of a computer. A curve representing the extent of departure from the ideal τ/τ_{1d} versus conversion x_A at a constant reagent feed rate is plotted. Also plotted is a curve showing the extent of departure from the ideal $\tau/\tau_{1\alpha}$ as a function of the velocity w of the reagents passing through the reactor at a particular percentage conversion x_A. Next, a curve showing the extent of departure from the ideal τ/τ_{1d} versus the linear velocity w at which the reagents pass through the reactor at constant x_A. Other calculations on a model with the aid of the computer involve the concentrations and conversions of NaOH and ethyl acetate over the length of the plug-flow reactor at known temperatures, initial NaOH and ethyl acetate concentrations, and reagent flow rates. The theoretical distribution of variables along the reactor is compared with the experimental one.

The report must include a schematic representation of the setup. The initial, experimental and calculated data are tabulated as follows:

Flow rate of 0.1 M NaOH, dm³/h ...
Flow rate of 0.1 M ethyl acetate, dm³/h ...
Overall reagent flow rate, dm³/h ...
Initial NaOH concentration C_{iNaOH} at the reactor inlet, mole/dm³ ...
Initial ethyl acetate concentration C_{iea} at the reactor inlet, mole/dm³ ...
Experimental temperature, °C ...

Distance from reactor inlet (reagent mixing point) to measurement point, cm	Reactor volume from inlet to measurement point, dm³	Reagent residence time τ, h	Concentration in solution, mole/dm³		Percentage conversion	
			C_{NaOH}	C_{ea}	x_{NaOH}	x_{ea}

Depending on the assignment, curves of changes in NaOH and ethyl acetate concentrations and conversions over the reactor length

are plotted along with the curve showing the extent of departure from the ideal τ/τ_{1d} versus the reagent conversion or flow rate. The results suggest the optimal process conditions.

B. BATCH PERFECTLY MIXED REACTOR

A batch reactor is characterized by simultaneous charging of the reagents into the reactor. The reagent concentration varies in time, however, owing to intensive mixing, it is the same throughout the reactor at a given point in time. The reagents stay in the reactor until their conversion reaches the desired level, after which the reactor is discharged then recharged, and the cycle is repeated. The duration of the reaction in a batch reactor can be measured directly (by a clock) since the process variables change in the course of time. To calculate the duration of the process in a batch reactor use is made of the equation

Fig. 90. Batch perfectly mixed reactor
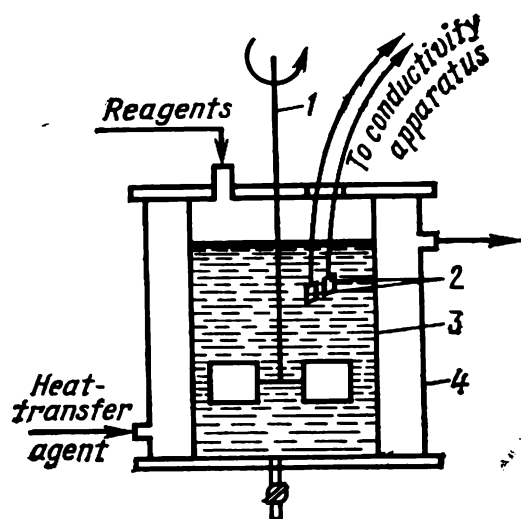
$$\tau = C_{A_0} \int_0^{x_A} \frac{dx_A}{-u_A} \quad \text{or} \quad \tau = \int_{C_{A_0}}^{C_A} \frac{dC_A}{-u_A}.$$

(3.102)

Knowing or given three values in Eq. (3.102), one can always calculate the fourth one.

This part of the work includes: (1) studying the reaction kinetics in a batch reactor; (2) application of the reaction kinetics in the selection and calculation of the reactors; and (3) determination of the effect of the reactor hydrodynamics on the process variables.

Experimental Setup and Procedure

The reactor (Fig. 90) is essentially a cylindrical glass vessel *3* with a stirrer *1*, inserted into another vessel *4* serving as a thermostat. The desired temperature is maintained by a continuous flow of water of a particular temperature from the thermostat into the jacket formed by the annular space between the vessels *3* and *4*. The temperature in the reactor is preset with the aid of a contact thermometer.

The reagents—0.1 *M* ethyl acetate and 0.1 *M* NaOH—are charged into the reactor through a hole in the lid of the latter. As the reaction

proceeds, the NaOH concentration is reduced. The change in NaOH concentration in the course of time is measured by a conductivity apparatus which determines the conductivity of the reaction mass. The lower the NaOH concentration, the higher the solution resistance. The alkali concentration at different instants is determined from the resistance value, and the results are used in analyzing the batch reactor performance.

The experiment is carried out as follows. The thermostat *4* is switched on. The desired temperature is preset by means of the contact thermometer. The necessary amount of 0.1 *M* ethyl acetate is poured into the reactor through a funnel, and the stirrer *1* is activated. The conductivity apparatus is prepared for measurements, and its electrodes *2* are immersed into the reactor. The reactor is rapidly filled with the specified amount of 0.1 *M* NaOH. A stopwatch is started the moment the reagents start being charged. The resistance of the reaction mass is measured by the conductivity apparatus. The four or five first measurements are taken at 30-40 s intervals, the subsequent ones, at 1 min intervals, and the final several measurements are taken every two minutes.

The assignments in this work include determination of changes in NaOH and ethyl acetate concentrations and conversions in the course of time at the specified temperature of 20°C. The starting solutions are 0.1 *M* ethyl acetate and 0.1 *M* NaOH. The experiments are carried out at alkali-to-ethyl acetate ratios of 1 : 2, 1 : 3, 1 : 4, and 1 : 5. The total reagent volume is 1 dm^3. Kinetic curves are plotted. The results are used to determine the rate constant and order of the reaction of ethyl acetate saponification with the alkali. The saponification is conducted at 20, 30, and 40°C, and the effect of temperature on its rate is determined. Next, the activation energy of the reaction is calculated. Also determined at one of the specified temperatures (20, 30, or 40°C) is the dependence of the reactor capacity on the NaOH conversion. The percentage conversion of NaOH may be 0.2, 0.3, 0.4, 0.5, 0.6, or 0.7. The reactor capacity is calculated using the formula

$$G = m/(\tau + \tau_{aux}),$$

where *G* is the reactor capacity with respect to one of the reaction products (sodium acetate), in mole/h; *m* is the amount of sodium acetate produced per run, in moles; τ is the operating time (duration of the reaction), in h; and τ_{aux} is the time spent on such auxiliary operations as charging and discharging of the reagents and products, startup and shutdown of the reactor, in h.

The report must include the diagram of the setup. The initial, experimental and calculated data must be tabulated as follows:

Volume of 0.1 *M* NaOH, dm³ ...
Volume of 0.1 *M* ethyl acetate, dm³ ...
Total volume of the solution, dm³ ...
Initial NaOH concentration in the reactor, mole/dm³ ...
Initial ethyl acetate concentration in the reactor, mole/dm³ ...

Elapsed time τ, s	Solution resistance R, ohms	Current solution concentration, mole/dm³		Percentage conversion		Reaction rate u, mole/(dm³× ×min)	Reaction rate constant k, dm³/(mole× ×min)
		C_{NaOH}	C_{ea}	x_{NaOH}	x_{ea}		

Curves representing changes in NaOH and ethyl acetate concentrations and conversions in the course of time are plotted. The results allow conclusions to be drawn as to the most efficient way to run the batch reactor.

C. CONTINUOUS PERFECTLY MIXED REACTOR AND A CASCADE OF REACTORS

Under steady-state conditions, all process variables in a perfectly mixed reactor are constant in time and in space (throughout the reactor volume). In calculations of a perfectly mixed reactor use is made of the following characteristic equation derived from the material balance of the reactor:

$$\tau = C_{A_0} x_A / (-U_A) \tag{3.103}$$

or

$$\tau = (C_{A_0} - C_A)/(-U_A). \tag{3.104}$$

In a single perfectly mixed reactor, the concentration of the starting reagents is low since it drops instantaneously to its final value. Therefore, the reaction rate and percentage conversion are small, too. To increase these parameters, a plurality of perfectly mixed reactors arranged in series, or a cascade of reactors, is used. The initial reagent concentration C_A in such an arrangement changes stepwise, the sharp change occurring instantaneously at the entrance of the reaction mixture into each reactor. For each reactor of a cascade, taken separately, the following equation for a single reactor, written for the nth reactor, is applicable:

$$\tau_n = (C_{A_{n-1}} - C_{A_n})/(-u_{A_n}). \tag{3.105}$$

The concentration C_A in the reactor cascade is higher than in a single perfectly mixed reactor and approaches in value, with a greater number of reactors in the cascade, that in a plug-flow

reactor. Therefore, to achieve the same conversion x_A, the total volume of the system decreases with increasing number of reactors in the cascade (at a constant cascade volume, x_A increases with the number of reactors).

To calculate the number of reactors in a cascade, necessary to achieve the specified conversion x_A, extensive use is made of the graphic method based on solution of a system of equations for each reactor in the cascade. One of them is the kinetic equation of the reaction

$$u_{A_n} = -k\Delta C_{A_n}. \qquad (3.106)$$

The other is the equation of a perfectly mixed reactor

$$u_{A_n} = (-1/\tau_n)\, C_{A_n} + C_{A_{n-1}}/\tau_n. \qquad (3.107)$$

Eq. (3.107) shows that the relation between the concentration of component A and the rate of its conversion in a perfectly mixed reactor is linear. Graphically, Eq. (3.107) represents a straight line with a slope equal to $-1/\tau_n$.

Determination of the number of reactors in a cascade (Fig. 91) calls for plotting of a kinetic curve representing $-u_A$ as a function of C_A (see Eq. (3.106)). Then, drawn from the point corresponding to the value of C_A is a straight line with $\tan \alpha = -1/\tau_n$, graphically representing Eq. (3.107). The point of intersection of the curve (3.106)
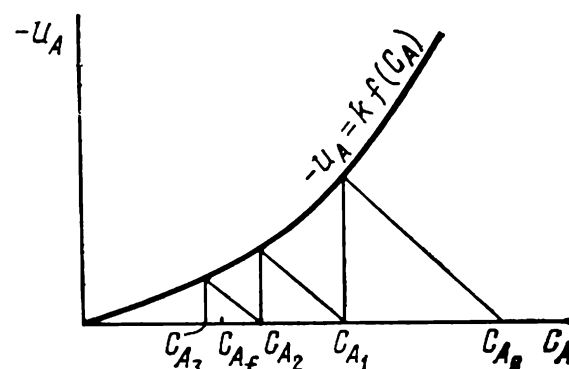
Fig. 91. Determination of the number of reactors in a cascade

with the straight line (3.107) corresponds to the value of concentration in the first reactor. Then, the concentration in the second reactor is determined, taking into consideration that the concentration in the first reactor is the initial one for the second reactor. Since τ_n is the same throughout the cascade, all straight lines defined by Eq. (3.107) are parallel. The above operations are repeated till the final concentration is obtained in one of the subsequent reactors.

This work includes: (1) studying the effect of the hydrodynamics of a continuous perfectly mixed reactor and a cascade of such reactors on the process variables; (2) application of the reaction kinetics in the calculations of a single perfectly mixed reactor and a cascade of such reactors; (3) studying the effect of the number of reactors in a cascade on the process results; and (4) determination of the extent of departure from the ideal in a single reactor and in a cascade under different operating conditions.

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Experimental Setup and Procedure

The starting reagents are fed into the reactor *14* or a cascade of reactors *11* through *14* (Fig. 92) from a thermostat *5* (0.1 *M* NaOH) or *6* (0.1 *M* ethyl acetate). The liquid level in the thermostats is maintained constant with the aid of controllers. To preset and control the temperature in the thermostats *5* and *6*, provision is made for contact
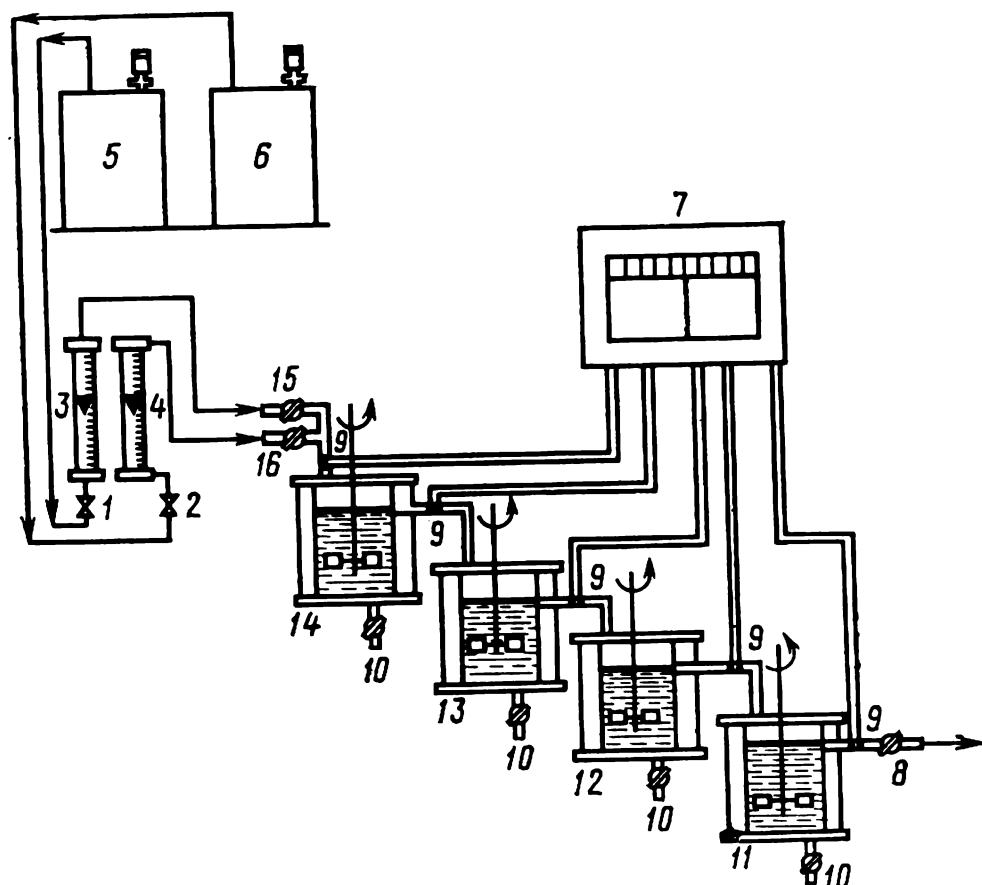
Fig. 92. Cascade of perfectly mixed reactors

thermometers. The reagents flow into the reactors *11* through *14* by gravity. The rate at which the reagents are fed into the reactor is adjusted by valves *1* and *2* with reference to rotameters *3* and *4*. The reagents are fed into the reactors at a specified rate. Valves *8*, *10*, *15*, and *16* in the reactor are intended to let the reagents in and out. To maintain a constant temperature in the reactor, it is enclosed in a jacket, in which a heat-carrier agent circulates at a particular temperature.

The NaOH and ethyl acetate solutions react as they pass through the reactor cascade. To determine the NaOH concentration, cells *9* with electrodes are arranged between the reactors, which measure the concentration by changes in the conductivity of the mixture, sensed by a KCM-4 instrument.

The experiment is conducted in the following sequence. The starting reagents, NaOH and ethyl acetate solutions, are poured into

the thermostats *5* and *6* with the valves *15, 16,* and *8* closed. The thermostats *5* and *6* are switched on, and the specified temperature is preset with the aid of the contact thermometers. The valve *10* is closed, and the valves *15, 16,* and *8* are opened. The NaOH flow rate is adjusted by the valve *1* with reference to the rotameter *3,* while that of ethyl acetate is adjusted by the valve *2* with **reference** to the rotameter *4.* Resistance measurements are taken by means of the KCM-4 meter in all reactors of the cascade, from which the NaOH concentration in the reaction mixture is determined. The experimental data are used in performance analysis of both a single continuous perfectly mixed reactor and a cascade of such reactors.

The reagent residence time is determined from Eq. (3.99). The ethyl acetate concentration is calculated from the initial concentration of this reagent and its amount entering into the reaction and equivalent to the amount of the reacted NaOH. The percentage conversion x_A of the reagent is determined from Eq. (3.100).

One of the assignments involved in this work is to determine the concentration or conversion of ethyl acetate or NaOH in a single perfectly mixed reactor or in a cascade of such reactors. In the experiments, the values of the following variables are changed: (1) reagent flow rate V (from 3 to 7 l/h); (2) ratio between the flow rates of NaOH and ethyl acetate $V_{NaOH} : V_{ea}$ (from 1 : 2 to 1 : 5); and temperature (from 20 to 40°C).

The reagent concentrations in the starting solutions (in the tanks) are: NaOH—0.1 mole/l; ethyl acetate—0.1 mole/l.

Curves representing the basic process variables, such as NaOH and ethyl acetate concentrations and conversions, as a function of the volume of a single perfectly mixed reactor or a cascade of such reactors are plotted. The effect of the reagent feed rate, ratio between the flow rates of NaOH and ethyl acetate, and temperature on the process variables is determined. Without changing the residence time, the reaction is conducted under the same conditions but with the number of reactors in the cascade being varied from one to four. (The residence time is maintained constant, with increasing number of the reactors, by increasing the reagent flow rate.) Also determined is the effect of the number of reactors in the cascade on the process variables. The process of ethyl acetate saponification in a single perfectly mixed reactor and in a cascade of such reactors is simulated. The mathematical model includes Eq. (3.105) for an ideal reactor and kinetic equation (3.101). The values of the rate constant are derived in an experiment with a batch reactor (see "Batch Perfectly Mixed Reactor") or taken from the literature.

The extent of departure from the ideal at a particular percentage conversion x_A is determined by comparing the residence time τ in a real reactor, calculated from the experimental data, with the residence time τ_{id} in an ideal reactor, calculated using a model on

a computer. The theoretical distribution of variables in a reactor and in the cascade, calculated with the aid of a computer using a model, is compared with the experimental one.

The report must include the diagram of the experimental setup, and the experimental and calculated data must be tabulated as follows:

Reactor number	Volume of n reactors	Residence time in a cascade of n reactors τ, min	Concentration in solution, mole/dm³		Percentage conversion	
			c_{NaOH}	c_{ea}	x_{NaOH}	x_{ea}

Curves showing changes in the NaOH and ethyl acetate concentrations and conversions as a function of the volume of a single reactor and the cascade are plotted. Also plotted are curves representing the extent of departure from the ideal τ/τ_{id} versus percentage conversion and flow rate of the reagents.

LITERATURE

Levenspiel, O., *The Engineering of Chemical Processes*, Moscow, 1969. *Chemical Technology*, Mukhlyonov, I. P., Averbukh, A. Ya, Tumarkina, E. S. *et al.*, 3rd revised and expanded edition, Moscow, 1971, Part I.

Instructions to the Laboratory Work "Analysis of Reactor Models"

1. Before the experiment, check the setup for air-tightness.
2. Use only diluted solutions in the experiment.
3. Activate the setup in the presence of the instructor or laboratory assistant.

Chapter 4

Electrochemical Processes

Electrochemical processes are those involving transformation of the electric to chemical energy or vice versa. The chemical energy transforms to the electric one in a storage battery, for example. The electric to chemical energy transformation takes place during electrolysis of solutions and melts, widely used in the chemical, metallurgical, metal-working, and other industries. The electrolysis of aqueous solutions of respective substances yields oxygen, hydrogen, chlorine, alkalis, hypochlorites, chlorates, perchlorates, permanganates, persulphates, hydrogen peroxide, and other inorganic compounds.

By electrolysis is meant decomposition of electrolytes, initiated by direct current and yielding new substances. When the electrodes are energized, the anions of the electrolyte move toward the anode, while the cations travel to the cathode. The chemistry of electrolysis resides in oxidation-reduction reactions at the electrodes. At the anode, anions give up electrons, that is are oxidized, while at the cathode, cations are reduced by taking up electrons. In this case, ions may discharge and form neutral substances in the solid, liquid, or gaseous state at the electrodes. If the anode is soluble in the electrolyte, the anions discharging at it cause anode cations (metal) to pass into solution.

Theoretically, of the several ions present in the electrolyte only the one[1] with the lowest electrode potential discharges at the electrode, which allows pure substances (e.g., metals) to be derived from their mixtures in the solution. The decomposition of the electrolyte always occurs in the liquid phase, although electrolysis as a whole often comprises the steps of formation of a new solid, liquid or gas phase, or dissolution of the solid anode, that is electrolysis is a heterogeneous process in the L-S, L-L, L-G, or L-S-G system*. In some industries, the replacement of purely chemical processes by electrolysis has made it possible to simplify the technology and to obtain inexpensive and pure products.

The main criteria of rational use of energy during electrolysis include current efficiency, energy consumption ratio, and energy consumption coefficient.

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* The systems are indicated without taking into consideration the electrodes which usually account for two more phases (S-S or S-L).

The *current efficiency* η is the ratio of the actual amount G of a substance produced in electrolysis to the theoretical amount G_{th} calculated from Faraday's law at the same electric power consumption. The current efficiency is expressed in fractions of unity

$$\eta = G/G_{th}. \tag{4.1}$$

The concept of "current efficiency" is similar to the well known concept of yield as percentage of the theory in a chemical process. The theoretical amount G_{th} of a substance can be calculated from a formula combining both Faraday's laws:

$$G_{th} = I\tau A/nF \text{ or } G_{th} = I\tau E, \tag{4.2}$$

where G and G_{th} stand for the amounts of produced substances, in g; I is the current intensity, in A; τ is the electrolysis time, in h; A is the atomic or ionic weight, in g; n is the ion charge; F is the Faraday constant corresponding to the theoretical amount of electric charge to be passed through the electrolyte to obtain one gramme-equivalent of the substance, in A/n; $F = 96\,500$ C/g.eq. or 26.8 A·h/g.eq; and E is the electrochemical equivalent, in g/A·h,

$$E = A/nF \tag{4.3}$$

By the *energy consumption ratio* μ is meant the ratio of the theoretical energy requirement w_{th} to the energy w actually consumed during electrolysis:

$$\mu = w_{th}/w. \tag{4.4}$$

The theoretical energy consumption (V·A·h or W·h) is calculated from the formula

$$w_{th} = v_{th}/\tau. \tag{4.5}$$

The theoretical bath voltage is

$$v_{th} = \varphi_a - \varphi_c, \tag{4.6}$$

where φ_a and φ_c are the equilibrium potentials of the anodic and cathodic reactions, respectively, in V.

The equilibrium potentials φ in Eq. (4.6) are calculated using the formula

$$\varphi = \varphi_0 + 2.3\,\frac{RT}{nF}\log C, \tag{4.7}$$

where φ_0 is the normal electrode potential; R is the gas constant, in J/(g.eq.·deg); T is absolute temperature, in K; n is the ion charge; F is the Faraday constant, in C/g.eq.; and C is the ion concentration (ionic activity).

For normal electrode potentials in aqueous solutions (at 25°C and ionic activity equal to unity) see Table 14.

Table 14

Electrodes	Electrode process	Normal potential, V
Cation-reversible	$K^+ + e \rightleftharpoons K$	−2.92
	$Na^+ + e \rightleftharpoons Na$	−2.71
	$Mg^{2+} + 2e \rightleftharpoons Mg$	−2.38
	$Al^{3+} + 3e \rightleftharpoons Al$	−1.66
	$Pb^{2+} + 2e \rightleftharpoons Pb$	−0.126
	$H^+ + e \rightleftharpoons 1/2H_2$	0.00
	$Cu^{2+} + 2e \rightleftharpoons Cu$	+0.34
	$Hg^{2+} + 2e \rightleftharpoons Hg$	+0.70
	$Ag^+ + e \rightleftharpoons Ag$	+0.80
Anion-reversible	$S + 2e \rightleftharpoons S^{2-}$	−0.51
	$1/2O_2 + H_2O + 2e \rightleftharpoons 2OH^-$	+0.40
	$1/2Cl_2 + e \rightleftharpoons Cl^-$	+1.36

The actual bath voltage v exceeds the theoretical value as a result of concentration and chemical polarization, as well as because of the ohmic resistances of the electrolyte and current leads. It is given by the formula

$$v = (\varphi_a - \varphi_c) + (\varphi_{a.conc} - \varphi_{c.conc}) + (\varphi_{a.chem} - \varphi_{c.chem}) + \sum IR, \quad (4.8)$$

where $(\varphi_{a.conc} - \varphi_{c.conc})$ is the voltage compensating for the concentration polarization and dependent on the degree of mixing of the electrolyte, current density, and temperature; $(\varphi_{a.chem} - \varphi_{c.chem})$ is the voltage compensating for the chemical polarization and dependent on the electrode material, current density, and temperature; and $\sum IR$ is the voltage drop across the conductors, due to their ohmic resistance $\sum R$.

The actual energy consumption (for calculation of μ using Eq. (4.4)) is

$$w = vI\tau/\eta. \quad (4.9)$$

Substitution of the value of w_{th} from Eq. (4.5) and w from Eq. (4.9) into Eq. (4.4) gives

$$\mu = (v_{th}/v)\,\eta. \quad (4.4a)$$

The *energy consumption coefficient*, that is the consumption of energy per unit electrolysis product, is determined from the formula

$$\beta = vI\tau/G, \quad (4.10)$$

β having the dimensions of $(V \cdot A \cdot h)/g$ or $(W \cdot h/g)$.

In industrial electrolysis of solutions, the current efficiency is often equal to 0.8-0.9. In melt electrolysis, usually $\eta < 0.8$.

The energy consumption ratio in solution electrolysis normally exceeds 0.5, while in melt electrolysis it is much lower. The energy consumption coefficients vary widely: for example, up to 2400 kW·h are consumed per ton of NaOH and up to 20 000 kW·h per ton of aluminium.

For practical studies of electrolysis, three laboratory works are included, which serve as typical examples of major electrochemical processes and are relatively easy to be carried out under laboratory conditions. They boil down to investigation of the effect of the basic process variables, such as process duration, electrolyte concentration, current density, electrolyte flow rate, electrode spacing, and others, on such electrolysis parameters as current efficiency, energy consumption ratio, energy consumption coefficients, product quality, and so on.

LABORATORY WORK 26. ELECTROLYSIS OF SODIUM CHLORIDE SOLUTION

The electrolysis of NaCl solution is the most typical example of an electrochemical process in an aqueous solution. It is also the simplest and most economic way to produce three valuable products—chlorine, hydrogen, and sodium hydroxide—within a single process from sodium salt which is a cheap and widely occurring raw material. At present, the production of chlorine, sodium hydroxide, and hydrogen by electrolysis of aqueous sodium salt solutions involves two techniques: diaphragm process with steel cathodes and mercury process with a mercury (liquid) cathode. No matter which process is used, the gaseous products—chlorine and hydrogen—are characterized by high concentration and purity. The mercury process yields the third product—sodium hydroxide which is also highly concentrated and chemically pure. All these advantages have contributed to the extensive application of the electrochemical process of chlorine production, which has totally supplanted chemical processes*.

Basic Electrode Processes. During electrolysis of an aqueous solution of NaCl, it is theoretically possible that the Na^+ and H^+ cations discharge at the cathode and the OH^- and Cl^- anions discharge at the anode. Whichever of these ions will in fact discharge at the electrodes and in which sequence depends, primarily, on the magnitude and ratio of the ion discharge potentials. The cathode is the site of hydrogen formation in accordance with the reaction

$$2H_2O + 2e = H_2 + 2OH^-. \qquad (a)$$
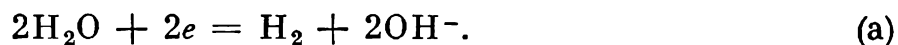
The discharge of sodium ions from aqueous solutions at a solid steel cathode is impossible because of the more electronegative potential

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* The electrolysis of a potassium chloride solution, yielding hydrogen, chlorine, and potassium hydroxide, is conducted in a similar manner.

of their discharge, as compared to hydrogen ions: ($\varphi_{H^+} = -0.415$ V; $\varphi_{Na^+} = -2.71$ V). The hydroxy ions remaining in the solution form, together with sodium ions, a solution of sodium hydroxide:

$$OH^- + Na^+ = NaOH. \tag{b}$$

At the anode, chlorine forms according to the reaction

$$2Cl^- = Cl_2 + 2e \tag{c}$$

although the equilibrium (reversible) potential of chlorine ion discharge in a saturated NaCl solution is higher than that of hydroxy ion discharge ($\varphi_{O_2(OH-)} = +0.82$ V; $\varphi_{Cl_2} = +1.32$ V). However, at carbon and graphite anodes, the OH^- ion discharge overpotential is much greater than that of Cl^- ions, which is why gaseous chlorine is predominantly released in accordance with reaction (c). The chlorine release is promoted by the increasing NaCl concentration in the starting solution as a result of the associated decrease in the equilibrium potential of Cl^- discharge. The overall electrolysis process can be written as

$$2NaCl + 2H_2O = Cl_2 + H_2 + 2NaOH$$

The side anodic reactions include liberation of oxygen

$$2OH^- - 2e = H_2O + 1/2O_2 \tag{d}$$
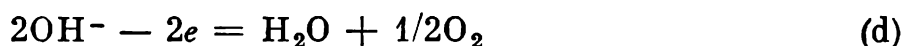
formation of carbon dioxide (in a reaction between the liberated oxygen and carbon of the anode)

$$C + O_2 = CO_2 \tag{e}$$

and formation of sodium chlorate

$$2Cl^- + 9H_2O = 2ClO_3^- + 1.5O_2 + 18H^+ + 18e. \tag{f}$$
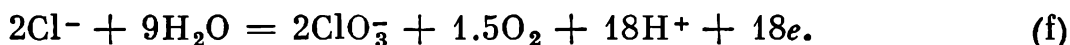
Proceeding in the solution are secondary reactions yielding sodium hypochlorite, chlorate and chloride:

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl; \quad HClO + NaOH = NaClO + H_2O$$
$$HCl + NaOH = NaCl + H_2O; \quad 2NaClO \rightleftharpoons NaClO_3 + 2NaCl$$
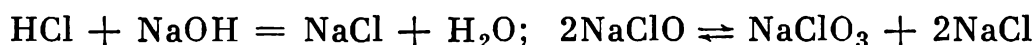
All these side processes bring down the current efficiency with respect to the main products, particularly oxidation of NaClO to $NaClO_3$ which consumes most of the electric current. To avoid or mitigate the secondary processes it is necessary to prevent the electrolysis products from mixing, therefore, the electrolyte is fed in countercurrent and a porous diaphragm separating the cathode and anode spaces is used.

Employed in the industry are baths with a filtering diaphragm closely adhering to a perforated steel cathode. A saturated NaCl solution is delivered through the anode space, is filtered through the porous diaphragm under hydrostatic pressure, and flows around the cathode. Thus, the electrolyte flows counter the OH^- ions toward

the anode, which hinders their penetration into the anode space and precludes side reaction. The cathodic product—a sodium hydroxide solution containing sodium chloride—is continuously removed from the cathode space. Another factor conducive to a higher current efficiency is the saturation of the initial electrolyte with NaCl (305 to 310 g/dm^3). Increasing the temperature up to 70-80°C permits lowering the bath voltage and decreasing the specific power consumption, as well as mitigating the side reactions by reducing the solubility of chlorine.

This work includes: (1) studying the electrochemical process of sodium hydroxide, chlorine and hydrogen production by electrolysis of aqueous solutions of sodium (or potassium) chloride on batch and continuous experimental setups; and (2) determination of such process parameters as current efficiency (electrolysis product yield) and electric power consumption coefficients.

Experimental Batch Setup and Procedure

The batch setup for electrolysis of sodium chloride solutions (Fig. 93) comprises a d-c power supply (e.g. copper-oxide rectifier)*,
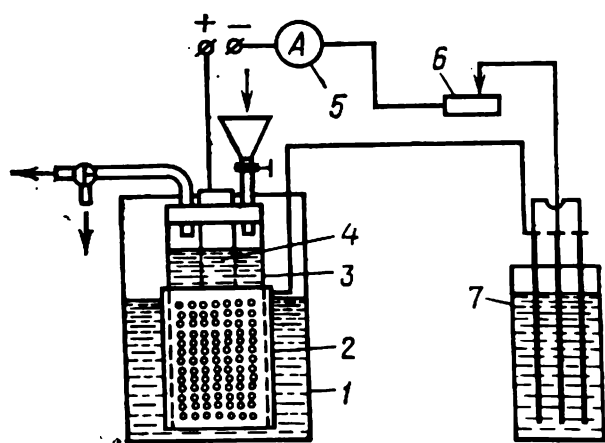
Fig. 93. Experimental setup for electrolysis of sodium chloride

a rheostat *6* to maintain direct current, an ammeter *5* with a 0 to 5 A scale reading to 0.1 A, a coulometer *7*, an electrolysis bath *1*, a gas holder connected to a three-way cock for sampling the anode gas, and a gas analyzer (the gas holder and gas analyzer are not shown).

The coulometer *7* is a rectangular glass vessel in which a copper plate serving as the cathode is suspended between two other copper plates serving as the anodes. The coulometer is filled to capacity with electrolyte which is an aqueous solution of copper sulphate with added amounts of sulphuric acid to enhance its conductance and ethanol to prevent the possible oxidation of copper. The meter is intended to determine the amount of electricity passing through the entire circuit from the increasing weight of the copper cathode, the current efficiency in the coulometer being almost 100% because of the absence of side processes. As current flows through the circuit, the copper of the coulometer anode passes into solution in the form

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* The rectifier supplies direct current to the board with the ammeter, rheostat, and positive and negative terminals.

of Cu^{2+} ions, while an equivalent amount of copper builds up on the copper cathode.

The electrolysis bath is essentially a glass vessel into which a cylindrical ceramic diaphragm *3* is immersed. The diaphragm permits separating the anodic products of electrolysis from the cathodic ones and partially eliminates the side reactions, that is interaction between sodium hydroxide and chlorine. A perforated steel cathode *2* is snug against the diaphragm. The anode and cathode spaces are filled with a prescribed amount of the electrolyte—a saturated NaCl solution. The anode space is closed tightly by a rubber plug inserted into which are a carbon anode *4*, a glass tube with a cock to remove chlorine from the anode space, and a funnel with a cock for charging the electrolyte.

A water-jet pump must be connected to the bath, associated through a hose with the anode space drain pipe via a surge bottle and a three-way cock. Prior to the experiment, the following preparations are to be made: (a) calculation of the carbon anode surface area (S dm^2) in the NaCl solution; (b) calculation of the current intensity necessary to achieve the desired anode current density D_a:

$$I = D_a S, \qquad (4.11)$$

where I is the current intensity, in A; D_a is the anode current density, in A/dm^2; and S is the surface area of that part of the anode which is immersed into the electrolyte, in dm^2; (c) cleaning the cathode with emery paper, washing it with water, drying, and weighing to within 0.1 g; (d) filling the coulometer with electrolyte to capacity and immersing copper electrodes into it; (e) filling the anode and cathode spaces of the bath with a specified amount of the saturated NaCl solution; (f) assembling the setup and testing it together with the instructor; (g) energizing the system with direct current, with the rheostat *6* being fully on, and adjusting the current by the rheostat with reference to the ammeter; and (h) conducting electrolysis for a specified period of time.

During electrolysis, gas samples are taken into the gas holder or directly into the gas analyzer for determining chlorine, carbon dioxide, and oxygen. The bath voltage is measured every 15 to 20 minutes. Samples are taken at definite intervals or after the experiment from the cathode space (5 to 10 cm^3 of the solution) to determine the actual amount of the formed sodium hydroxide by titration with 0.1 N HCl in the presence of phenolphthalein. The current efficiency is calculated from the amount of the produced sodium hydroxide, using Eq. (4.1).

The theoretical amount G_{th} is calculated from Eq. (4.2). To this end, the amount Q of the electricity passed through the circuit is determined with the aid of the coulometer (by the weight increment of the copper cathode), and the result is compared with the calculated

value. These data and the actual bath voltage measured by a voltmeter* are used to calculate the energy consumption coefficient per kg of the product (sodium hydroxide), using Eq. (4.10).

The yield of chlorine is determined from the results of analysis of the gas from the anode space. The anode gas contains the following components:

1. Chlorine resulting from the basic anodic process—discharge of Cl^- ions.

2. Oxygen resulting from the discharge of OH^- ions at the anode according to reaction (d).

3. Carbon dioxide resulting from interaction between carbon anodes and oxygen.

The gas analysis comprises two main steps: sampling and analysis proper. For the analytical procedure and gas analyzer design see Work 36.

The analysis of a given gas mixture forming in the anode space of the electrolysis bath is performed with the aid of a gas analyzer consisting of three absorption vessels: the first vessel is filled with a sodium hyposulphite solution for absorption of chlorine; the second vessel contains a 33% solution of potassium hydroxide for absorption of carbon dioxide; and the third vessel is filled with an alkaline solution of pyrogallol to absorb oxygen. In the course of analysis, it is important to follow the absorption sequence, that is the gas is first transferred (at least 6 to 8 times) from the measuring burette into the first vessel for absorption of chlorine, then into the second vessel for absorption of carbon dioxide (6 to 8 times) and, finally, into the third vessel for absorption of oxygen (at least 15 to 18 times). If this sequence is not observed, the analysis will yield erroneous results since the alkaline solution of pyrogallol also absorbs carbon dioxide.

To take a gas sample, the gas holder** filled with a saturated solution of NaCl is connected to the anode space drain pipe through a three-way cock and a hose. The middle and lower cocks of the gas holder are opened to let out the liquid dropwise into a beaker. At least 250 cm^3 of the gas must be taken in a sample. If the sampling is done directly into the gas analyzer, the first 100 cm^3 of the gas are used to be blown through the glass manifold of the gas analyzer and the hose to remove the remnants of the previous sample.

The preparation of the gas analyzer for analysis involves a procedure whereby the liquid in the absorption vessels is raised to the marks on the capillaries by means of a levelling bottle. Then, the measuring burette is filled with the liquid, through a three-way

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* Taken for calculations is the mean bath voltage (averaged over measurements at the beginning, in the middle and at the end of the experiment).
** The total volume of such a gas holder is about 0.5 dm^3.

cock, up to the top mark on the capillary. The system is tested for air-tightness of all rubber joints and cocks. Before sampling, the glass manifold must be washed with the analyzed gas to displace the air it contains. For this purpose, 15 to 20 cm^3 of the gas are taken from the gas holder into the burette and vented into the atmosphere through the discharge branch of the three-way cock, the level of the liquid seal in the measuring burette being brought up to the upper mark on the capillary (up to zero).

Next, the burette is made to communicate, through the three-way cock, with the gas holder (the levelling bottle is raised to the upper mark of the measuring burette), and as the levelling bottle with the liquid is slowly lowered, the gas is displaced into the burette (100 cm^3). When more than 100 cm^3 of the gas are taken, the excess is carefully vented into the atmosphere, after which the burette is disconnected from the atmosphere and gas holder by the three-way cock. To determine the chlorine content, the gas is transferred into the vessel with sodium hyposulphite and back into the burette with the cock of the vessel open. The gas is transferred by slowly raising and lowering the levelling bottle. Such pumping is repeated six to eight times, then the level of the absorbing solution is brought up to the mark, the cock is shut, and the volume of the remaining gas is measured with the liquid in the measuring burette and levelling bottle being at the same level. This operation is repeated until the volume of the remaining gas stops changing. The chlorine volume v is calculated from the difference $v = v_0 - v_1$, in which v_0 is the sampled gas volume (100 cm^3), and v_1 is the volume of the gas remaining after absorption of chlorine. The contents of carbon dioxide and oxygen are then determined in a similar manner.

Care must be taken to avoid penetration of any one of the absorbing solutions into the glass manifold or measuring burette. In case of contamination, the manifold and burette must be immediately disconnected and washed, while the liquid seal in the levelling bottle must be replaced by a fresh solution. After the experiment, the remaining gas is vented into the exhaust hood. The absorbing solutions and liquid seal are brought up to respective marks on the capillary, and the gas analyzer is handed over to the laboratory assistant in the state of readiness for the next analysis. The cathode of the coulometer is washed with a water jet, dried in a drying cabinet, and weighed. The electrolyte of the coulometer is decanted into a special bottle. The setup is handed over to the laboratory assistant.

Example of calculation of the chlorine yield. The following reactions take place at the anode:

$$2Cl^- = Cl_2 + 2e$$
$$2OH^- = H_2O + 1/2 O_2 + 2e$$
$$O_2 + C = CO_2$$

Let the gas be of the following composition (vol.%): Cl_2 $a = 90$; CO_2 $b = 3$; O_2 $m = 2$; N_2 $q = 5$ (the latter is what remains after analysis). The chlorine yield is calculated using the formula

$$100 - \eta = \frac{2(b+m)}{a + 2(b+m)} \cdot \qquad (4.12)$$

Eq. (4.12) holds, provided no air is present in the gas sample. However, since air is almost invariably present in the gas (because of the anode space not being airtight and as a result of the process being of a batch nature), an appropriate correction factor must be introduced. The air composition is as follows (approximately): 79% of nitrogen and 21% of oxygen, that is 3.76 volumes of nitrogen per volume of oxygen. In the analysis, nitrogen is determined from the gas remaining after absorption of Cl_2, CO_2, and O_2, provided the absorption of these gases has been complete. In our example, the nitrogen content is 5%. Hence, the corresponding amount of oxygen is

$$3.76 - 1O_2$$

$$n = \frac{5 \cdot 1}{3.76} = 1.33,$$

$$5 - nO_2$$

hat is the amount of air in this gas is $5 + 1.33 = 6.33\%$.

Then, the component content is calculated on the assumption of an airless gas mixture:

$$Cl_2 = \frac{90}{100 - 6.33} \, 100 = 96.08\%;$$

$$CO_2 = \frac{3}{100 - 6.33} \, 100 = 3.20\%;$$

$$O_2 = \frac{2 - 1.33}{100 - 6.33} \, 100 = 0.72\% \cdot$$

The total is $96.08 + 3.20 + 0.72 = 100\%$.

Next, the chlorine yield is calculated from Eq. (4.12)

$$100 - \eta = \frac{2(3.2 + 0.72)}{96.08 + 2(3.2 + 0.72)} \, 100 = 7.84\%,$$

$$\eta = 100 - 7.84 = 92.16\%.$$

Hence, the yield of chlorine is 92.16%.

The experimental and calculation results are entered in the following tables:

| Amount of electrolyte, cm³ | | Anode surface area S, dm² | Anode current density D_a, A/dm² | Current intensity I, A | Weight of coulometer copper cathode | | Amount of separated copper G', g | Mean bath voltage v, V | Amount of sodium hydroxide, g | | Yield of NaOH η, % | Energy consumption coefficient β, kW·h/kg |
cathode space	anode space				before exp.	after exp.			theoretical G_{th}	actual G		

Sample number	Sampling time from the beginning of electrolysis	Composition of anode gas, vol. %			Chlorine yield η, %
		chlorine	carbon dioxide	oxygen	

Knowledge of the chlorine and alkali yields, energy consumption coefficients for these products, and bath voltage gives a better insight into the electrolysis process.

The report must include the schematic of the setup and the diagram of connection of the instruments. Added to the description of the assignment must be an explanation of the processes involved in electrolysis and a table with the experimental data. In addition, the calculations of the chloride and sodium hydroxide yields must be included together with that of the energy consumption coefficient.

Experimental Continuous Setup and Procedure

In the industry, electrolysis baths operate on a continuous basis, which is why studying electrochemical processes on continuous laboratory setups is of particular interest. The experimental continuous setup for electrolysis of a NaCl solution is illustrated in Fig. 94.

The electrolysis bath comprises a body *8* fashioned from acrylic plastic together with the lid *13*. Secured to the body and lid with

Fig. 94. Continuous bath for electrolysis of sodium chloride

the aid of steel tie rods *7* is the tapered bottom *1* of the bath, accommodating a slip ring *2*, a perforated iron cathode *3*, a horizontal asbestos diaphragm *4*, and a rubber gasket *5* making the joint airtight. The cathode adheres closely to the diaphragm from below. Inserted
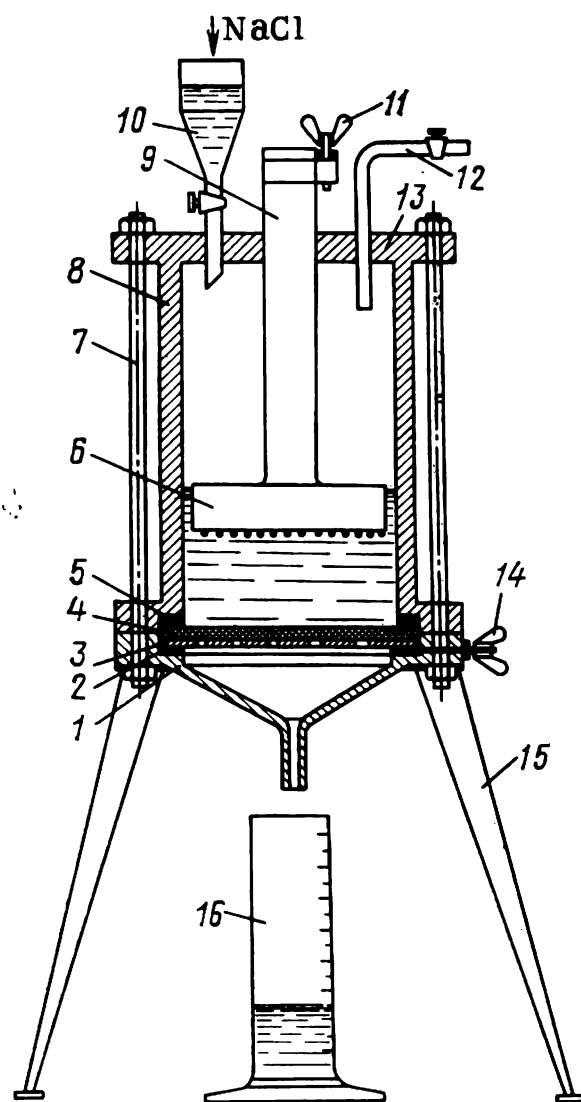
into the holes of the lid are a funnel *10* for a saturated NaCl solution to be continuously fed into the electrolysis bath, a carbon anode *9* with a horizontal disc *6*, and a glass tube *12* with a cock for removal of chlorine. Current is applied to the terminals *14* (cathode lead) and *11* (anode lead). The bath is mounted on a support *15*; put under the discharge pipe is a measuring vessel *16* for collecting the product— sodium hydroxide solution—forming continuously at the cathode during filtration of the electrolyte through the diaphragm and cathode.

The filtering asbestos diaphragm is prepared by depositing an asbestos compound onto the cathode. To this end, 20 to 30 g of asbestos are ground and heated with water till a uniform paste is formed. The resulting paste is aspirated (deposited) with the aid of a Büchner filter and a water-jet pump onto the iron cathode which is essentially a round perforated plate or a mesh.

Fig. 95. Continuous setup for electrolysis of sodium chloride

For the diaphragm to be stronger, it is recommended to first put a piece of cloth (of the same shape as the cathode) on the cathode and then apply the asbestos paste. Similar pieces of cloth should be placed on top of the diaphragm when excess moisture is sucked off it. The moist diaphragm is ready for use.
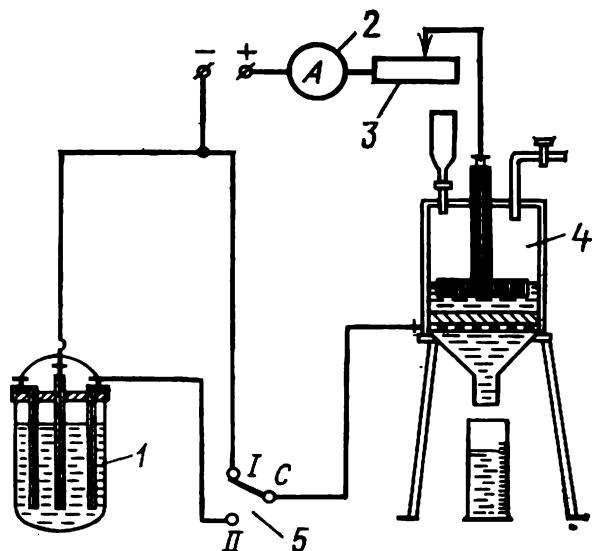
The continuous setup is shown shematically in Fig. 95. It consists of the electrolysis bath *4*, a coulometer *1*, a switch *5* intended for changeover from the bath to the coulometer after the bath operation has stabilized, a rheostat *3*, and an ammeter *2*. The bath voltage is measured by a portable voltmeter. Before the experiment, a saturated NaCl solution is poured into the bath through the funnel *10* (Fig. 94) in an amount sufficient for the liquid to cover the working disc-shaped portion of the carbon anode over three fourths of its height. Then, the brine starts being continuously fed into the bath, its flow rate being controlled by the cock of the funnel *10* so that the level of the electrolyte in the bath remains constant. The electrolyte is filtered through the diaphragm and cathode and discharged into a receiver. After that, the switch is set to position *I*, and direct current is applied after its intensity has been adjusted with the aid of the rheostat *3* (Fig. 95) and ammeter *2*. To stabilize the bath operation, electrolysis is conducted for 30 to 40 minutes under the specified conditions, then the liquid flowing out of the cathode space of the bath starts being sampled (for analytical procedure see below).

If the NaOH content in two or three samples is constant, the switch K (Fig. 95) is positioned at II, the stop-watch is started, and the cathode liquid is quantitatively collected in the graduated vessel *16* which is placed instead of the solution receiver used during the bath stabilization period (see Fig. 94).

In the steady state, the anode gas is analyzed at predetermined time intervals for the contents of chlorine, carbon dioxide, and oxygen, and the differential yield of chlorine is calculated using Eq. (4.12) During the experiment, the bath voltage is measured two or three times by the portable voltmeter. The electrolysis is brought to an end after the bath has operated under steady-state conditions over a certain period of time. This is done in the following sequence: the stopwatch is stopped, the direct current supply is cut off, the graduated vessel *16* is replaced by another receiver, and the volume of the cathode liquid in it is determined. The weighing of the copper cathode of the coulometer is followed by measurement of the amount of electricity that passed through the electrolysis bath during the experiment, and the theoretical amount of NaOH (G_{th}) is determined from Eq. (4.2).

The cathode liquid from the receiver *16* is analyzed by titration of a 10-cm^3 sample with 0.1 N HCl in the presence of phenolphthalein to determine the concentration of sodium hydroxide in the cathode liquid from the formula

$$C_{NaOH} = vm0.004 \cdot 1000/10, \qquad (4.13)$$

where v is the amount of 0.1 N HCl spent in the titration of the sample, in cm^3; m is a correction factor for reducing the titre exactly to 0.1 N HCl; 0.004 is the amount of NaOH, corresponding to 1 cm^3 of 0.1 N HCl; and C_{NaOH} is the concentration of the analyzed solution, in g/dm^3.

With the concentration and total volume of the analyzed cathode liquid known, the actual amount of sodium hydroxide formed at the cathode during electrolysis (G) is determined, then the total yield η of sodium hydroxide is calculated using Eq. (4.1). The current efficiency in continuous electrolysis can also be calculated using a formula derived from the material balance of a process with flow electrolyte. In this case, the calculation of the current efficiency using Eqs. (4.1) and (4.2) is simplified. If the concentration of sodium hydroxide (lye) is expressed in terms of gramme-equivalents in one litre and related to the hourly consumption of the lye, substitution of G_{th} from Eq. (4.2) into Eq. (4.1) gives

$$\eta = C_{NaOH}LF/I, \qquad (4.14)$$

where η is the current efficiency; L is the lye flow rate, in dm^3/h; C_{NaOH} is the concentration of NaOH in the lye, in g.eq./dm^3, F is the Faraday constant equal to 26.8 A-h/g.eq.; and I is the current intensity, in A.

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The lye flow rate is determined from the volume of the outflowing cathode liquid and duration of the experiment. Then, the energy consumption coefficient is calculated per gramme of sodium hydroxide from Eq. (4.10).

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Applied Electrochemistry, Alabyshev, A. F., Vyacheslavov, P. M., Galbnek, A. A. *et al.*, 3rd revised and expanded edition, Leningrad, 1974.

Chemical Technology, Mukhlyonov, I. P., Averbukh, A. Ya., Kuznetsov, D. A. *et al.*, 3rd revised and expanded edition, Moscow, 1977, part II.

Instructions to the Laboratory Work "Electrolysis of Sodium Chloride Solution"

1. When pouring electrolyte into the coulometer, do not splash it on your clothes and hands because it contains sulphuric acid.

2. Check, together with the instructor, whether the setup has been assembled correctly. Make sure that the electrodes have been positioned properly in the coulometer (the cathode must be arranged between the anodes strictly in parallel), the conductors are thoroughly insulated, and the position of the switch during operation of the continuous setup is correct (position *I* during the startup period, and position *II* during operation).

3. Switch on the d-c supply only in the instructor's presence with the rheostat used to control the current intensity being fully on.

4. Before the system is energized, start the water-jet pump for drawing off chlorine when the water flows in a narrow stream.

5. Do not bend over the bath during electrolysis and by no means check the aspiration of gases by smelling for chlorine may cause intoxication and affect the mucous coat of the respiratory tract.

6. Since hydrogen is released from the cathode space, **it is strictly forbidden to hold a flame—from the burner, heater, etc.—near the setup.**

7. Students are not allowed to discharge the electrolyte from the anode space. After the experiment, the bath must be handed over to the laboratory assistant.

8. Sample the cathode liquid for analysis **only with the aid of a rubber syringe** to avoid ingestion of the toxic solution.

LABORATORY WORK 27. ELECTROLYSIS OF LEAD CHLORIDE MELT

The electrolysis of melts is extensively employed in modern industrial practice as the only way to produce light and alkali metals: aluminium, sodium, calcium, beryllium, magnesium, and some of their alloys. For this purpose, melts of salts, oxides, hydroxides, or their mixtures are used. For example, sodium is obtained through electrolysis of NaCl or NaOH, magnesium is produced by electrolysis of carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$, aluminium is electrolyzed from alumina dissolved in cryolite Na_3AlF_6, and beryllium, from beryllium chloride mixed with sodium chloride, and so on.

Since electrolysis of melts is conducted without water and at a high temperature (resulting from the heat released when direct

current passes through the electrolyte), it has some specific features when compared with electrolysis of aqueous solutions. These specific features govern both the industrial process and electrolysis on an experimental setup in a laboratory. In melt electrolysis, the energy of the electric current is spent to melt the electrolyte, decompose the substance, and compensate for heat losses. The process is carried out at temperatures ranging widely from 310 to 1400°C. The lower temperature limit is due to solidification of the electrolyte or metal. Therefore, for electrolysis to be conducted at lower temperatures, use is made of complex mixtures forming low-melting point eutectics. As a result, metals are produced primarily in a molten state.

The current efficiency is reduced as a consequence of evaporation of the electrolysis products, occurrence of side reactions, dissolution of metals in the molten salt, and dissolution of the anodic product in the melt. The effect of metal evaporation on the current efficiency is relatively insignificant in most processes in view of the fact that electrolysis is conducted at as low temperatures as possible. Only in some cases, for example, electrolysis of molten $CdCl_2$, the evaporation of the cathodic product is the leading factor responsible for losses. The most tangible losses of electrolysis products occur as a result of solubility of the cathodic and anodic products, their diffusion toward each other, recoalescence of the substance decomposed during electrolysis, oxidation of the molten metal with the atmospheric oxygen, and other side processes.

Each system is characterized by equilibrium between the melt and metal at a particular temperature, responsible for some extent of the latter's passage into the electrolyte in the dissolved state. If, for some or other reason, the dissolved metal is removed from the melt, the equilibrium is upset, and a new portion of the cathodic metal passes into the melt, whereby the current efficiency is reduced. As the temperature increases up to a certain limit, the amount of the metal passing into the melt increases, too.

The cathodic metal is lost due to dissolution of the metal near the cathode, diffusion of the dissolved metal toward the anode, and consumption of the dissolved metal near the anode (oxidation). The first two processes have nothing to do with the current density but depend on temperature, the shape and size of the electrolyzer. Therefore, the current efficiency will increase with the current density because the absolute amount of the formed metal increases with more or less constant losses. As far as the electrolyzer shape and size are concerned, the former affects the rate of back diffusion and convection, while the latter bears on the absolute amount of dissolved metal losses.

A specific feature of electrolysis of molten salts is the "anodic effect" which manifests itself when the normal course of electrolysis is suddenly upset by an abrupt surge of the bath voltage (20 to

50 times exceeding the rating) with a simultaneous drop in current intensity. This effect stems from the fact that at high anode current densities, particularly in the case of carbon anodes, there takes place accumulation of gases separating the anodes from the melt by a nonconducting layer. The resulting "gas pocket" interrupts the normal flow of current. The current density at which the "anodic effect" usually takes place depends on the electrolyte type and temperature. The effect can be temporarily eliminated by raising the anodes and stirring the melt, that is by taking measures which do not disturb the gas film surrounding the anode.

Melt electrolysis is also characterized by high energy consumption and low values of the energy consumption coefficient. The main reason for that is the high ohmic resistances of the buses, contacts, and, primarily, electrolyte whose heating to the required elevated temperatures is accomplished by the energy of direct current.

To study the process of melt electrolysis, lead chloride is subjected to it on a laboratory setup. This work includes studying the process of melt electrolysis, determination of the current efficiency as a function of process temperature at a constant current density and as a function of the latter at a constant temperature, as well as determination of the amount of energy consumed per kg of the product which in this case is lead.

Experimental Setup and Procedure

The experimental setup for electrolysis of lead chloride (Fig. 96) comprises a d-c source, a rheostat *2*, an ammeter *1* with a 0 to 5 A scale reading to 0.1 A, a coulometer *3* (described on p. 316), a crucible furnace *4* to melt the electrolyte and maintain the specified electrolysis temperature, an electrolysis bath *5* consisting of a large porcelain crucible accommodating two carbon electrodes *6* and *8* with their upper portions enclosed in protective porcelain tubes, and a small porcelain crucible *7* forming the cathode space and accommodating an electrode *6* serving as the cathode, a thermocouple *9*, and a galvanometer *10* for measuring the electrolyte temperature.

The electrolyte is lead chloride with potassium or sodium chloride added to lower the melting point of the electrolyte. The amount of the addition is determined from the melting-point diagram of the $PbCl_2$-KCl (Fig. 97*a*) or $PbCl_2$-NaCl (Fig. 97*b*) mixture. As can be seen from Fig. 97*b*, the mixture containing 73 mol. % of $PbCl_2$ and 27 mol. % of NaCl melts at 410°C, that is at a temperature 80°C lower than the melting point of pure lead chloride. When 20 mol. % of potassium chloride are added to lead chloride, the mixture melts at 405°C (Fig. 97*a*).

Before the experiment, specified amounts of $PbCl_2$ and KCl (or NaCl) are weighed on a counter balance, based on 180 to 200 g of

the charge. Then, the salts are intimately mixed in a porcelain mortar. The large porcelain crucible, or electrolyzer *5*, is mounted into the furnace (Fig. 96), in which the small crucible, or cathode space,
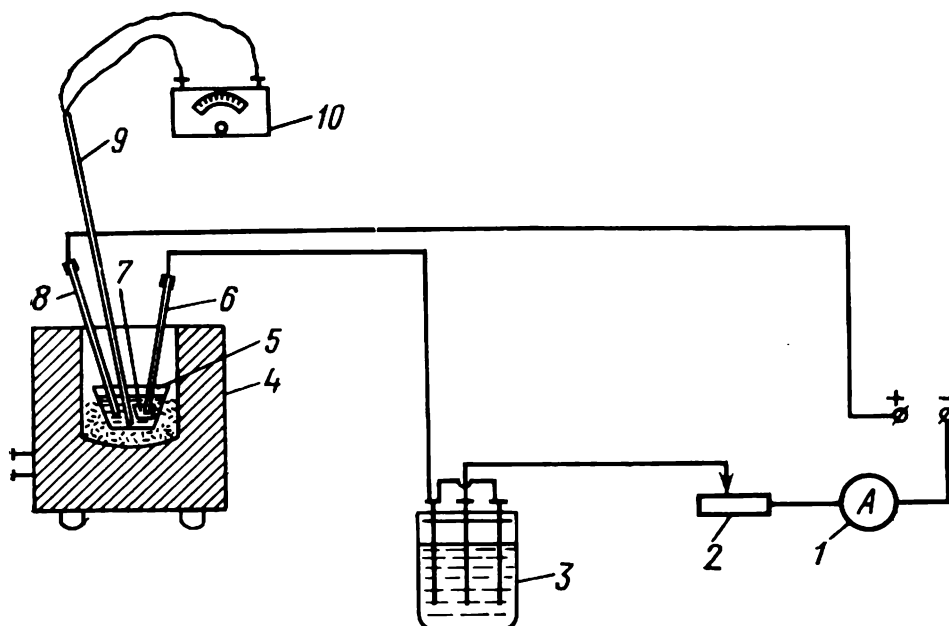
Fig. 96. Experimental setup for electrolysis of lead chloride

is placed. A graphite electrode, or cathode *6*, is lowered all the way to the bottom of the small crucible. Another graphite electrode, or anode *8*, is inserted into the anode space together with the thermo-
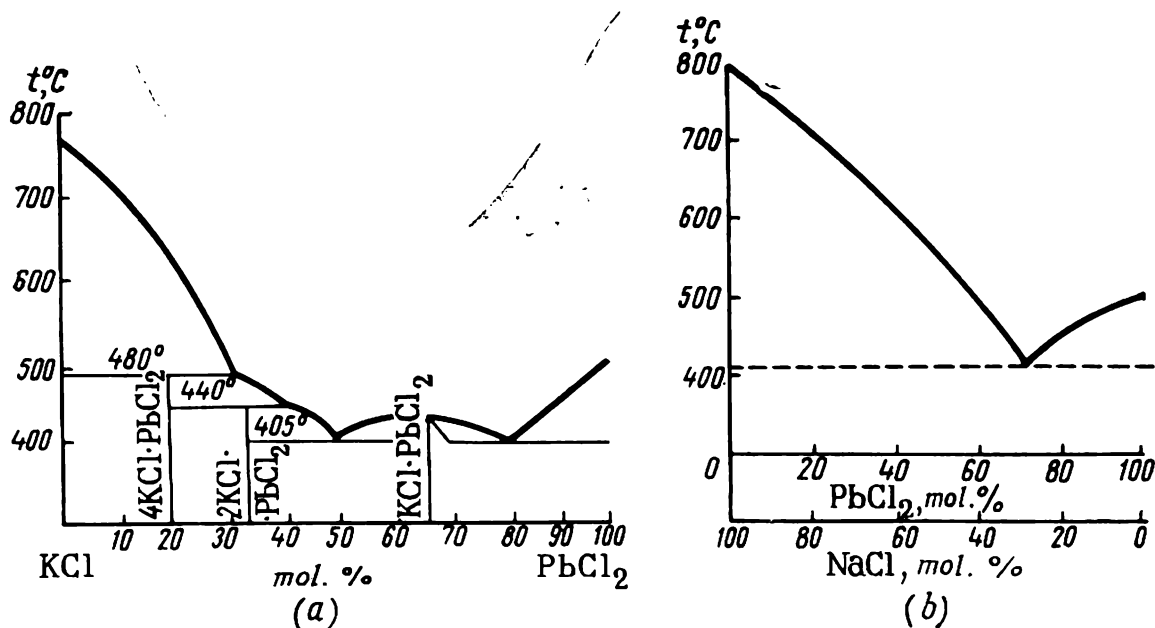
Fig. 97. Melting-point diagram
a—KCl-PbCl₂ system; *b*—NaCl-PbCl₂ system

couple *9*. The electrodes and thermocouple are secured in an upright. The electrolyzer is then filled to capacity with the prepared mixture of salts, and the crucible furnace covered by asbestos board is energized. Next, the electric part of the setup is assembled. After the

electrolyte has melted and the required temperature has been reached, the setup is checked in the instructor's presence, the d-c supply is switched on, and electrolysis is conducted under the specified conditions. In the course of electrolysis, the voltage across the bath electrodes is measured by a portable voltmeter every 15 to 20 minutes.

After the experiment, the d-c supply is switched off, the anode and cathode are withdrawn from the electrolyte (raised on the upright) and preheated tongs are used to remove the porcelain crucible with metallic lead from the furnace. The contents of the crucible are transferred into a preheated porcelain cup, and, after the electrolyte has cooled, the lead "button" is cleaned. The final cleaning of the button from the adhering electrolyte is done by boiling it in distilled water. Then, the button is dried and weighed. At the same time, the dried cathode of the coulometer is weighed. The cleaned and weighed lead button is handed over to the instructor.

The small porcelain crucible free of the electrolyte and lead is immediately reinserted by the tongs into the large crucible, or electrolyzer, the electrodes are reinserted, too, the current is adjusted (or temperature, depending on the assignment), and the d-c supply is switched on for the second experiment; the experiments are repeated in the same sequence as many times as may be required. The electrolyte level in the crucible is maintained by adding an appropriate amount of the salt mixture so that it is 7 to 15 mm above the upper edge of the small porcelain crucible placed on the bottom of the large one serving as the electrolysis bath. After the experiment, the electrolyte is transferred into a porcelain cup. The experimental data are used to calculate the current efficiency on the basis of Eqs. (4.1) and (4.2) and the energy consumption coefficient on the basis of Eq. (4.10).

The experimental results and calculated values are tabulated as follows:

Experiment number	Charge composition		Current density, A/m²	Current intensity, A	Temperature, °C	Electrolysis time, min	Weight increment of the coulometer cathode, g	Amount of electricity passed trough bath, A·h	Lead yield, g	Bath voltage v, V	Current efficiency η, %	Energy consumed per kg of lead β, kW·h/kg
	PbCl₂	KCl (NaCl)										

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A Practical Course in Applied Electrochemistry, Ed. by Kudryavtsev, N. T. and Vyacheslavov, P. M., Moscow-Leningrad, 1973.

Instructions to the Laboratory Work
"Electrolysis of Lead Chloride Melt"

1. Carry out the experiment under an exhaust hood, and handle the electrolyte wearing protective gloves.

2. Thoroughly check the assembled setup together with the instructor.

3. Lower the electrodes all the way to the crucible bottom (the small crucible must be on the bottom of the large one).

4. Charge the salt mixture so that the small crucible is completely submerged in the melt.

5. Switch on the current only in the instructor's presence, with the rheostat being fully on.

6. Carefully wrap the upper part of the crucible furnace in asbestos sheets.

7. Be especially careful when withdrawing the small crucible; handle it with tongs held by gloved hands, and transfer its contents into a preheated porcelain cup. Bear in mind that as the electrolyte solidifies, it tends to crack, and the detached pieces may touch your face and hands.

8. Protect the electrolyte and electrolyzer against moisture.

9. Hand over the produced and weighed lead button to the instructor.

LABORATORY WORK 28 CHROMIUM PLATING OF METALS

For protection of metal articles against corrosion, giving them a nice untarnished appearance, protection of rubbing components of machines and instruments against wear, and imparting improved conductance or certain optical properties to the surface of metal articles, they are plated with zinc, chromium, copper, nickel, and other metals.

Metals must be prepared for plating with extreme care. In doing so, it must be remembered that cleanness of the surface to be plated is a prerequisite for close adherence and nice appearance of the protective and decorative coating. Metal surfaces are usually contaminated with oxides (rust), dust, greases, and other substances. Before plating, the metal surface must be cleaned and rendered smooth and bright. The preparation of surfaces for plating includes the following steps: mechanical cleaning, degreasing, pickling, and dipping. The mechanical cleaning of large articles and structures consists in blasting the surface with a jet of sand delivered by compressed air. In some cases, sandblasting is applied to small articles as well. Another technique involves blasting surfaces with small steel shots. The most critical parts are machined on grinders by abrasive then flexible wheels prior to plating. This type of treatment cleans the surface and removes burrs, pits, and other surface irregularities. Steel brushes are also used for cleaning (scratch brushing).

The removal of lubricants and greases is done by treating the surface with organic solvents (kerosene, petrol, benzene, dichloroethane, etc.) and alkaline solutions (e.g., 5-10% solution of NaOH). Electrochemical degreasing in alkaline solutions is also used. In this case, the cleaning process is promoted by emulsification of the oil

and grease by gas (hydrogen or oxygen) bubbles. Advanced techniques include ultrasonic treatment which provides for quick separation of the contaminants from the surface. It is also carried out in alkaline solutions or organic solvents, which is particularly effective in the cleaning of very small components.

The pickling is done to remove oxides from the metal surface. Ferrous metals are normally pickled in sulphuric and hydrochloric acids, while nonferrous ones are pickled in sulphuric, hydrochloric and nitric acids. Electrochemical pickling consists in anodic or cathodic treatment in an electrolyte of a particular composition under given conditions. The final step of preparation for plating is dipping, or mild pickling. This process is aimed at removal of extremely thin oxide films often invisible to the naked eye and forming on the already prepared surfaces (during transportation or short-term storage). The dipping is done immediately before articles are immersed into the plating bath and is the final step of preparation for plating. The deposition of thin (down to fractions of micrometres) coats is performed by the following main techniques: (1) hot-dip process—dipping an article into a molten metal for a short period of time with the result that a protective metal film is formed on the article; (2) thermomechanical process (cladding), which is based on hot rolling of both the protected and protecting metals together; (3) sputtering (metallization), which consists in spraying a molten metal over the surface of the article being protected with the aid of compressed air or an inert gas; and (4) the most important process of electroplating of ferrous metals with thin films of nonferrous metals to protect the former against corrosion and give them a nice appearance (decorative coating).

Plated coatings are normally produced by deposition of a nonferrous metal on the article during electrolysis of aqueous solutions of respective salts. In this case, the article being plated serves as the cathode on which cations of the metal are deposited in a thin smooth and, as a rule, lustrous layer. The source of the coating metal may be a plate made of it, serving as the anode and dissolving in the electrolyte. Also used are anodes insoluble in the electrolyte, with a solution of a salt of the coating metal being added to the bath as the metal is being spent.

A big advantage of the electroplating process is the easy control of the latter, insofar as the coating thickness is concerned. Other advantages include absence of heat, which means that the metal structure does not change and the metal itself does not deform. Plated coatings have a good lustre, which is why they are often deposited for decorative purposes. Plated coatings, however, are not dense enough to fully protect the metal against corrosive liquids; ions of solutions penetrate through pores in the coating and attack the metal.

Distinction is made between anodic and cathodic coatings. If the electrode potential of the coating metal is lower (i.e. the latter is more electronegative) than that of the coated one, the coating is said to be anodic, and dissolving in the electrolyte is the coating metal. In the case of cathodic coating, the protected metal is attacked through pores or discontinuities in the coating. Zinc coating is anodic with respect to steel. On the other hand, copper, chromium, nickel, tin, and lead form cathodic coatings.

To obtain a closely adhering and nice looking coating, the surface must be clean, therefore, it must be thoroughly prepared. To rid the surface of scale, burrs, and other irregularities, it is blasted with a jet of quartz sand or tiny shots, then ground by abrasive wheels and cleaned by wire brushes. For complete removal of oxides from the metal surface, pickling with weak solutions of sulphuric or hydrochloric acid is widely used. Lubricants and greases are removed by treatment with diluted alkaline solutions and such organic solvents as kerosene, petrol, benzene, dichloroethane, and others.
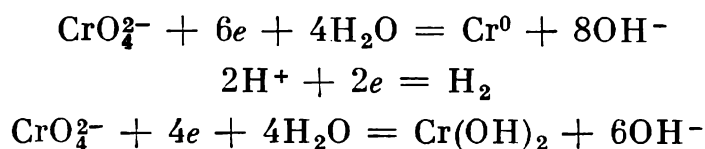
At present, electric chromium plating is one of the most commonly used processes. Chromium is a steel-gray bright metal with a bluish tint, chemically stable and characterized by high strength and wear resistance. It belongs to electronegative metals ($\varphi_{Cr/Cr^{3+}} = -0.67$ V), however, it has a strong tendency for passivation, which brings it closer to noble metals in terms of stability. For example, exposure to organic acids, sulphur, hydrogen sulphide, sulphur dioxide, nitric acid, and alkaline solutions produces practically no effect on the metal. However, chromium is not stable in reducing media, solutions of chlorides, sulphuric and hydrochloric acids. It is stable in a humid atmosphere and retains its lustre for a long period of time because the highly transparent passive film on the chromium surface protects the metal against tarnishing. The oxide film also prevents chromium from rapid oxidation, which is why it reliably protects steel articles even at elevated temperatures (800 °C). Being chemically stable, chromium coatings are nevertheless porous and do not provide reliable protection against corrosion, for in the galvanic pair iron-chromium the latter will be the cathode. In view of this, to minimize the porosity, a coat of copper and nickel is applied before chromium plating. In this case, the thickness of the chromium layer is small—0.8 to 1 μm. Electrolytic chromium exhibits high hardness which exceeds that of carbon steel, as well as a low friction coefficient, heat resistance, and chemical stability, which makes chromium-plated components highly wear-resistant. Chromium plating is extensively used to enhance the wear resistance of measuring tools, gauges, cutting tools (drills), moulds, and rubbing parts of various instruments and machines (in the manufacture of aircraft engines, it is used in the fabrication

of cylinders and piston rings). Chromium plating is also used in the production of reflectors and to give decorative finish to various: parts.
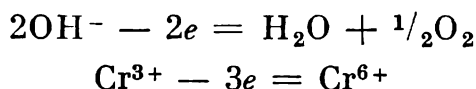
Chromium is deposited from an electrolyte whose basic component is chromium oxide CrO_3 rather than a chromium salt as in most of other electroplating processes. An aqueous solution of chromium (VI) oxide is a strong acid. Electrolysis in CrO_3 solutions involves insoluble anodes made of a lead alloy with 5 to 6% of antimony. It is not recommended to use soluble anodes of metallic chromium because their dissolution produces ions of various degrees of oxidation, which disturbs the bath operation; in addition, the anodic efficiency is six to eight times greater than the cathodic one, which causes accumulation of chromium in the electrolyte.

The chromium plating process is characterized by an extremely low cathodic efficiency (8 to 16% in terms of Cr^{6+}). The major portion of the electric energy is spent in side processes: electrolysis of water and reduction of Cr^{6+} to Cr^{3+} at the cathode, and oxidation of Cr^{3+} to Cr^{6+} at the anode. It is assumed that the following basic processes occur at the electrodes:

at the cathode

$$CrO_4^{2-} + 6e + 4H_2O = Cr^0 + 8OH^-$$
$$2H^+ + 2e = H_2$$
$$CrO_4^{2-} + 4e + 4H_2O = Cr(OH)_2 + 6OH^-$$

at the anode

$$2OH^- - 2e = H_2O + {}^1/_2O_2$$
$$Cr^{3+} - 3e = Cr^{6+}$$

Premium chromium deposits are possible only if the electrolyte contains sulphuric acid of a particular concentration or its salts. Reducing the sulphuric acid concentration in chromium (VI) oxide solutions results in evolution of hydroxides and spoils the deposit on the cathode. Raising the H_2SO_4 concentration lowers the cathodic efficiency because according to the equilibrium equation

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$
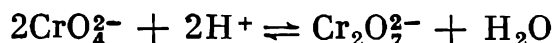
the concentration of CrO_4^{2-} necessary for deposition is reduced. The presence of a small amount of SO_4^{2-} in the electrolyte is beneficial because they yield, together with Cr^{3+}, soluble compounds and impede the formation of hydroxides. The content of sulphuric acid must correspond to the ratio $CrO_3 : H_2SO_4 = 100$-200.

At low CrO_3 concentrations, the current efficiencies are maximum but the bath voltage increases. Greater CrO_3 concentrations involve a lower current efficiency and substantial losses of the electrolyte. This is why it is common practice to use solutions of medium concentrations, containing 150 to 250 g/dm^3 of CrO_3.

Temperature and current density produce a tangible effect on the current efficiency. It decreases with increasing temperature and increases with the current density. Both factors are interrelated. Corresponding to each temperature is a particular range of current densities at which bright chromium deposits are obtained. Lower current densities produce matte, or "milky", deposits, while the higher ones result in gray deposits. If the current density is too low for a given temperature, practically no deposition of chromium takes place, and only side processes occur. As the temperature decreases, the cathodic efficiency increases but the range of current densities for bright deposits becomes narrower, and the deposits become more brittle. Therefore, the electrolyte temperature is normally not lower than 45°C.

Temperature and current density also strongly affect the basic property of electrochemical chromium—its hardness. By varying the electrolysis conditions one can obtain chromium deposits of different hardness. Bright chromium deposits are characterized by dense crazing. Matte deposits are not crazed. For protective and decorative purposes, bright deposits should preferably be obtained directly from the electrolyte.

Protective and decorative chromium coatings are applied on parts made of steel, copper, brass, and aluminium. Since bright chromium is highly porous, steel articles are first coated with copper and nickel to ensure their corrosion resistance. The deposition of copper and nickel is performed in the copper-nickel-chromium or nickel-copper-chromium pattern. Bright chromium coatings can be deposited directly from the electrolyte only if the deposition is done on a polished surface. The total thickness of the copper and nickel layer is 15 to 45 μm, the chromium layer being 1 to 2 μm thick. To deposit bright chromium for protective and decorative purposes, use is made of an electrolyte having the following composition: CrO_3 250 g/dm^3 H_2SO_4 2.5 g/dm^3, and the following optimal conditions: cathode current density—10 to 25 A/dm^2; electrolyte temperature—45 to 49°C.

An alternative to the multilayer copper-nickel-chromium coating is the deposition of matte chromium of low porosity directly on steel. The composition of the electrolyte may be the same as in protective and decorative chromium plating, but the process is conducted at 70°C and a cathode current density of 25 to 35 A/dm^2. It is also common to resort to combined, matte and bright duplex chromium plating. The latter is recommended for articles exposed to high humidity. This type of chromium plating is conducted successively in two baths with electrolytes of the above-mentioned compositions. First, matte chromium is deposited at 70°C and a cathode current density of 30 A/dm^2, then the part is transferred (without rinsing) into the second bath where bright chromium is deposited at 50°C and a current density of 30 to 50 A/dm^2.

When chromium plating is performed to improve wear resistance, the chromium deposits are 300 to 900 μm thick. In this case, no copper and nickel sublayer is used. Wear-resistant chromium coatings are applied on new machine components and tools subject to intensive wear during operation, as well as to restore worm parts. In this case, the electrolyte usually contains 200 to 230 g/dm^3 of CrO_3 and, accordingly, 1.9 to 2.1 g/dm^3 of H_2SO_4. The process is conducted at 55°C and a cathode current density of 35 to 40 A/dm^2 or at 67°C and a current density of up to 100 A/dm^2.

This work is concerned with the process of electric chromium plating and the effect of temperature and current density on the current efficiency and appearance of the deposited chromium.

Experimental Setup and Procedure

Before proceeding to the experiment, one must make some calculations in accordance with the assignment. Electroplating processes are characterized by current efficiency, quality of the product, particularly thickness of the coating, and bath voltage. The current efficiency is calculated in accordance with Faraday's laws using Eq. (4.1).

In the case of chromium, the electrochemical equivalent is $E = 0.323$ g/A·h, hence the current efficiency for an electric chromium plating bath is

$$\eta = G/I\tau 0.323. \tag{4.15}$$

The second process parameter to be calculated—chromium coating thickness—is determined from the formula

$$\delta = \tau D_c \, \eta/22.3, \tag{4.16}$$

where δ is the coating thickness, in μm; D_c is the cathode current density, in A/dm^2; τ is the electrolysis time, in h; η is the current efficiency; and 22.3 is the ratio of the chromium density (7.2 g/cm^3) to its electrochemical equivalent (0.323 g/A·h).

Eq. (4.16) can be used to determine the chromium plating time τ, necessary to attain the required coating thickness δ.

To carry out the experiment it is necessary to: (1) prepare specimens for coating and weigh them on an analytical balance; (2) calculate the cathode (specimen) surface area; (3) calculate the current intensity from the specified cathode current density; and (4) determine the required chromium plating time from Eq. (4.16).

By preparation of the specimens is meant cleaning and degreasing of their surface. To do this, several specimens (in accordance with the assignment) in the form of separate plates are numbered and thoroughly cleaned with emery paper till their surface becomes smooth and bright. After the specimens have been wiped clean with

filter paper, they are degreased in an organic solvent, then swabbed with a paste (a mixture of chalk with soda, or a chrome paste: chromium oxide 80%, stearin 15%, oleic acid 5%) and properly rinsed with running water. While a specimen is being degreased, its surface must not be touched with fingers. A properly prepared specimen surface is completely wettable with water. The specimens dried at 110 to 120°C are weighed on an analytical balance and stored in an exiccator.

The chromium plating is carried out on a setup shown schematically in Fig. 98. The chromium plating bath *7* is in this case an ordinary
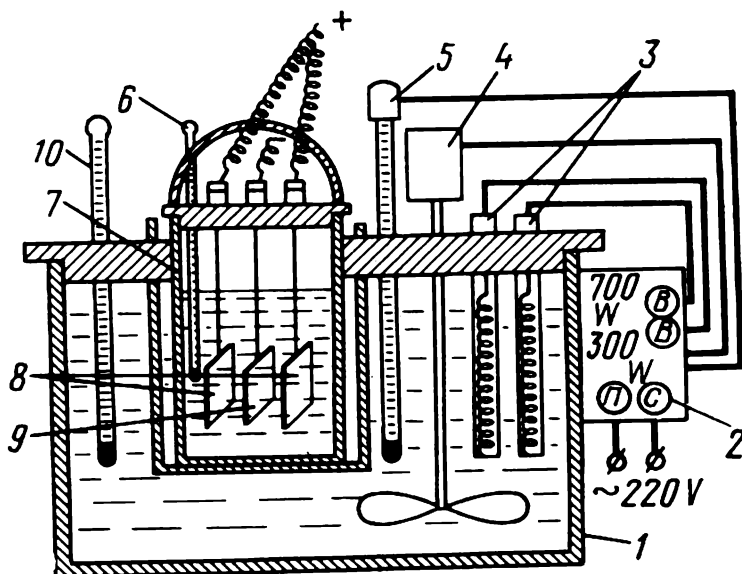
Fig. 98. Experimental setup for chromium plating

porcelain cup having a capacity of one litre. The lid of the bath accommodates conducting anode and cathode clamps and a thermometer *6*. The anodes *8* and cathode *9* are secured in the clamps on the lid by means of a special support (not shown). The anodes are two specially fashioned lead plates 16 × 36 mm in size with a conducting stem. The cathode is a steel plate (20 × 40 mm) also with a conducting stem. The anode and cathode leads must be insulated by PVC tube. The cathode is arranged between the two anodes in parallel to their surface. It is not recommended to hold the anodes and cathode in the chromium electrolyte without current because the passive films forming on lead and steel conduct current poorly or not at all. The chromium bath is heated with the aid of a water thermostat *1*. Arranged on its cover are two heating elements *3* rated at 700 and 300 W, an electric motor with a stirrer *4*, a contact thermometer *5*, and a test thermometer *10*. The 300-W heater is intended to boost the heating. After the specified temperature has been reached, the 300-W heater is switched off, and the temperature is controlled by the 700-W heater.

The temperature is regulated by the contact thermometer *5* with magnetic adjustment. The contact thermometer is set to the desired temperature as follows: the horseshoe magnet is turned for course adjustment of the temperature with reference to the upper scale of the thermometer. The fine adjustment is done by turning the magnet, with reference to the test thermometer, and registering the instants at which the heater comes on and off. The electrically driven stirrer *4* and heaters *3* are energized by the switches on the control panel *2*.
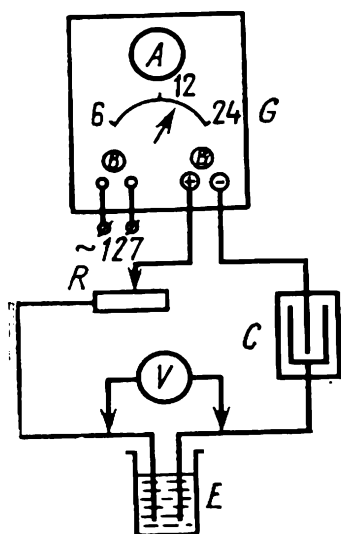

Fig. 99. Connection of instruments during chromium plating

To energize the thermostat, it must be connected to an a-c (220 V) supply, then the heater switches (B) must be set to position "on", and the button "start" (П) must be depressed. The thermostat is de-energized by depression of the button "stop", (C). It takes one to one and half hours for the thermostat to be heated.

After all the preparatory work and the associated calculations have been completed, one must assemble the electric circuity for energizing the instruments used in chromium plating (Fig. 99). It comprises the electrolysis bath *E*, a voltmeter *V*, a coulometer *C*, a gas-filled thermionic-diode rectifier *G**, and a rheostat *R*. All the circuit components are connected in series, except for the voltmeter which is connected in parallel with the electrolyzer at definite time intervals.

Arranged on the front panel of the rectifier *G* are a-c and d-c switches, an ammeter *A*, and the transformer arm positioned at 6, 12, or 24 V. The position at which the transformer arm is set depends on the intensity of the consumed direct current, the voltage being increased with the current intensity.

The coulometer *C* is a standard instrument for determining the actual amount of electricity passing through the system. The mean value of this amount can, of course, be determined from the product of the current intensity *I* by time τ. Sulphuric acid is added to the electrolyte of the coulometer to enhance its conduction, and alcohol is added to prevent the reaction $2Cu^+ \rightarrow Cu^{2+} + Cu$. Before the experiment, the copper cathode of the coulometer is cleaned with emery paper and weighed on an analytical balance. The amount of electricity is calculated from the weight increment of the copper cathode after the electrolysis is over, the current efficiency in the copper coulometer being taken equal to 100%.

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* If the rectifier is not available, a d-c source is used.

Before the system is energized, the assembled circuitry must be shown to the instructor. It is energized by application of alternating current to the gas-filled thermionic-diode rectifier G with a-c switches being in the "on" position. The thermionic diode of the rectifier takes two to three minutes to be warmed up. Then, the d-c switch must be set to position "off", and the required current intensity must be preset with the aid of the rheostat R and voltage transformer.

In the course of electrolysis, the current intensity and temperature must be maintained constant and the bath voltage measured. After the experiment, the d-c supply must be switched off, the lid with the electrodes must be removed from the chromium plating bath, and the electrodes must be thoroughly washed with running water. The chromium-plated specimen must be dried at 110 to 120°C and weighed on the analytical balance. The copper cathode of the coulometer must also be washed with running water, dried, and weighed.

The appearance of the chromium coating (bright, matte, or gray) is assessed visually, the coating thickness is calculated using Eq. (4.16), and the current efficiency is determined from Eq. (4.15). The coating porosity may be determined by the dye penetration method. The dye penetrant for iron is a solution containing 10 g/dm^3 of $K_3[Fe(CN)_6]$ and 20 g/dm^3 of NaCl. Filter paper soaked with this solution is placed on the surface of the chromium-plated specimen, cleaned in advance with paste and lime and rinsed with water. The appearance of blue dots on the paper is indicative of the presence of pores in the coating. The experimental and calculation results are tabulated as follows:

Composition and amount of electrolyte, g	Specimen dimensions, mm × mm	Specimen surface area S_1, dm^2	t, °C	Specimen weight, g		Specimen weight increment, G_1-G_0, g	Plating time τ, h	Cathode current density D_c, A/dm^2	Current intensity I, A	Coating thickness δ_1, μm	Current efficiency η, %
				before plating, G_0	after plating, G_1						

LITERATURE

Applied electrochemistry, Alabyshev, A. F., Vyacheslavov, P. M.,Galnbek, A. A. *et al.*, 3rd revised and expanded edition, Leningrad, 1974.

A Practical Course in Applied Electrochemistry, Ed. by Kudryavtsev, N. T. and Vyacheslavov, P. M., Leningrad, 1973.

Instructions to the Laboratory Work
"Chromium Plating of Metals"

1. Carry out all experiments with chromium electrolyte and chromium (VI) oxide only under an exhaust hood and wearing rubber gloves.

2. Protect the skin and clothes against electrolyte splashes.

3. Carefully watch the) insulation of all leads and the position of the electrodes in the electrolyzers (the cathodes must be arranged in parallel with the anodes).

4. Check the assembled electric circuitry with the instructor or laboratory assistant.

5. Do not hold an open flame (burner, heater) near the bath because of the intensive liberation of hydrogen and oxygen during electrolysis.

6. Switch on the bath in the instructor's presence.

Chapter 5

Preparation of Raw Materials and Material Analysis Techniques

The quality of a raw material and, particularly, the concentration of the valuable component in it are the major factors determining its processing technique and the product quality. Therefore, it is essential adequately to prepare raw materials used in the chemical industry, especially dress (concentrate) them and remove the noxious impurities they contain.

The techniques of concentrating the basic component in raw materials differ fundamentally for solids, liquids, and gases. Solid mineral raw materials (ores) can be concentrated mechanically or chemically. The chemical methods based on the capacity of raw material components to interact with various reagents are highly specific and are applied directly at chemical plants processing a particular raw material. At dressing plants, the initial preparation of raw materials involves primarily mechanical processing: sifting (screening), gravity separation, electromagnetic and electrostatic separation, and flotation. Flotation of ores is one of the most widely used ways of concentrating them on a large scale. The process of flotation also makes an interesting object of study because it involves a wide variety of physicochemical phenomena. It can easily be simulated under laboratory conditions.

Water is extensively used in chemical industry. It is involved almost in all processes, usually in large amounts and for diverse purposes. The consumption of water in various processes amounts to tens, hundreds, and even thousands of cubic metres per tonne of the product. Depending on the process in which water is used, different requirements are imposed on its purity, and accordingly various water purification and treatment techniques are recommended. In most cases, the water used for process purposes is softened, that is freed of Ca^{2+} and Mg^{2+} ions. One of the most effective ways to soften water is to pass it through a granulated cation exchanger bed (see Work 30).

Knowledge of raw material and product analysis techniques as well as process monitoring procedures is a prerequisite for managing and improving production. The methods of analysis and comprehensive investigation of semiproducts and products are to a great extent determined by the phase composition of the reacting systems.

Consequently, this chapter includes works dealing with anaylsis of solid, liquid and gaseous mixtures of various components as well as heterogeneous binary systems. Both chemical and physical methods of analysis and testing are applicable to all systems under investigation.

Automation and computerization of chemical production makes it particularly important to develop and implement rapid analysis and testing techniques based, as a rule, on the use of sophisticated instrumentation. The instruments, in which measurements of physical variables or analysis of the chemical composition are combined with electronic signal conditioning and display of the data, include porosimeters, instruments for measuring the surface area of porous materials, electron microscopes, derivatographs, spectrophotometers, chromatographs, gas analyzers, and other advanced instruments whose application is described in this chapter.

LABORATORY WORK 29. FLOTATION

Flotation is used to separate complex sulphide ores, separate apatite from nepheline, as well as dress coals and numerous minerals for the manufacture of various chemicals.

Flotation is based on different wettability of minerals with water. Figure 100 illustrates the position of wettable (hydrophilic) and
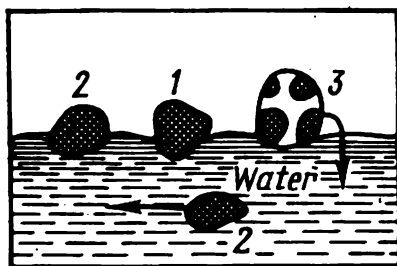
Fig. 100. Flotation phenomena

unwettable (hydrophobic) particles of a mineral in water during flotation. The surface tension forces tend to smooth out the liquid level with the result that the hydrophobic particles *1* are ejected from the liquid (float up), while the hydrophilic particles *2* sink. The smaller the particles, the greater the ratio of their surface to volume (and mass) and the more pronounced the wetting. Small hydrophobic particles rise to the water surface regardless of density. The flotation efficiency is increased by a number of techniques—comminution to break the links between the crystals of different minerals and to develop the particle surface; vigorous stirring and passing air bubbles through the pulp; addition of special substances known as flotation agents to promote more complete separation of minerals by flotation, and so on.

To this end, small air bubbles are passed upward through the mixture of solid pulverized minerals with water. In this case, the hydrophobic mineral particles adhere to the air bubbles *3* and are carried by them to the water surface to form a froth on the latter, which is collected in special receivers (launders or chambers). The froth spontaneously disintegrates in these receivers, and the resulting solid residue forms what is known as the *flotation concentrate.*

The hydrophilic mineral particles do not adhere to the air bubbles but remain suspended in the liquid. In the course of time, they settle to the bottom of the flotation cell and accumulate there in the form of a precipitate known as *tailings.* Since the froth formed by the air stream is unstable and quickly disintegrates, frothing agents are introduced into the pulp, which are essentially surfactants forming adsorption films on the surface of air bubbles. The frothing agents include pine oil, wood and coal tar, some high-molecular alcohols, and other substances.

Fig. 101. Pneumatic flotation cell

1—air supply (air flow indicated by arrows); *2*—mineralized froth; *3*—concentrate launder; *4*—concentrate discharge; *5*—circulation compartment with pulp; *6*—tailings discharge

Naturally occurring minerals differ in wettability but insignificantly, which is why *collecting agents* (*collectors*) are introduced into the pulp, that is substances that are readily adsorbed on some minerals, coating their surface with a hydrophobic film, and are not adsorbed on others. The *collecting agents* include oleic acid, naphthenic acids, xanthates, and the like. In the case of complex ore flotation, the collecting and frothing agents used provide for flotation of several, rather than one, minerals present in the ore. Therefore, in order to float one mineral and keep another from flotation, to the pulp are added *conditioning agents* which enhance either the hydrophobic properties of the particles, imparted by the collector, (activators) or the hydrophilic properties (inhibitors). Thus, repeated selective* flotation of a complex ore yields a number of concentrates floating with the froth, while what ultimately stays under water is gangue. The use of highly active flotation agents minimizes their consumption at a concentration plant, which in some cases does not exceed 100 g per tonne of ore. In a laboratory, where more readily available agents are used, their consumption rate is much higher. The ore to be separated by flotation is crushed then finely ground (to a particle size not larger than 0.1 to 0.3 mm). The ground ore and water with flotation agents are fed into the flotation cell. Two
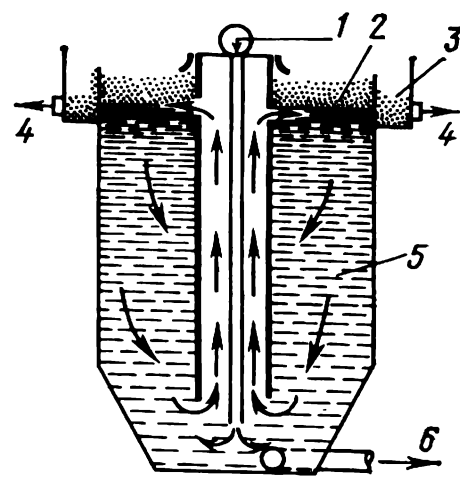
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* By selective is meant successive flotation of one component after another from a complex ore.

types of flotation cells are employed: mechanical and pneumatic. A pneumatic cell is shown schematically in Fig. 101.

Ground ore is fed into the pulp and agitated by the same air that causes hydrophobic particles to rise to the surface. Air emerges from a common manifold through pipes, in the form of bubbles. As the bubbles rise up the middle narrow portion of the cell, they entrain the pulp and the froth whose density is much lower than that of the water in the surrounding space. This causes intensive circulation of the pulp. The hydrophobic particles together with air bubbles form, on the pulp surface, a layer of mineralized froth which is discharged through launders as it accumulates. The froth disintegrates forming a residue containing the concentrate of the valuable mineral. The concentrate is separated from water in settlers and on filters, then dried with hot flue gases or air.

The tailings are removed in the form of a slurry from the bottom portion of the cell. In the case of multiple flotation, the slurry, to which appropriate agents are added, undergoes the next stage of selective flotation.

The efficiency of a flotation process depends on a number of factors of which the most important are: (1) characteristics of ores and coals (properties of individual constituent minerals, their ratios, the presence of impurities, conditions of mineral formation, etc); (2) fineness of the floated mineral particles; sufficient flotation rate and selectivity can be attained by optimizing the granulometric composition on conformity with a particular average particle size; if the particles are too small, the flotation rate and selectivity are adversely affected, while large particles remain in the tailings; (3) ratio between the solid (S) and liquid (L) phases of the pulp. It is standard practice to determine the optimal $S : L$ ratio in each process experimentally; raising the temperature intensifies the flotation process, although the effect of temperature on various flotation agents is different; (4) presence of impurities in the flotation water, the presence of various ions in the pulp may activate the process, but it may also produce a negative effect; and (5) range of the available flotation agents, their consumption rate, time of contact between the agents and water, and the order in which they are added. Usually conditioning agents are added first to adjust the pH of the pulp, then inhibitors followed by collectors and, finally, frothing agents, this sequence, however, may vary from case to case.

This work is concerned with flotation of some minerals.

Experimental Setup and Procedure

The laboratory flotation setup shown schematically in Fig. 102 comprises a flotation cell *1* mounted on a frame *2*. The cell consists of two communicating compartments: agitation *(A)* and separa-

tion (*B*). The motor *3* driving the agitator *6* is also mounted on the frame. The amount of air aspirated by the cell is measured by a rheometer *5* associated with the restrictor valve *4* of the air line.

A weighed amount of ground and screened ore is placed in the agitation compartment of the cell, water is poured on it, and the appropriate flotation agents are added. The weight ratio between the solid and liquid phases in the pulp varies from 1 : 5 to 1 : 3. The agitator is switched on, and air starts being supplied. The resulting froth with the concentrate flows over into the separation compartment where the flotation process is completed. The froth with the concentrate is transferred, with the aid of a skimmer (not shown), into a beaker *7* secured on the frame. The tailings settle to the bottom.

The concentrate and tailings are filtered, dried at 120 to 130°C, and weighed. Below examples of flotation of some commercial minerals are given.

Fig. 102. Experimental flotation cell with pneumatic and mechanical agitation

Flotation of Apatite-Nepheline Ore. This ore contains the following compounds: fluorapatite $3Ca_3(PO_4)_2 \cdot CaF_2$; nepheline (Na, K)$_2O \cdot Al_2O_3 \cdot 2SiO_2$; chlorapatite $Ca_3(PO_4)_2 \cdot CaCl_2$; hydroxylapatite $Ca_3(PO_4)_2 \cdot Ca(OH)_2$; carbonate-apatite $Ca_3(PO_4)_2 \cdot CaCO_3$, and other minerals containing $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3.

Flotation is the first step of processing of this multicomponent and valuable raw material. Calcium phosphates used in the production of phosphorus, phosphoric acid, and phosphoric fertilizers are separated in the course of flotation from nepheline which is a raw material for the production of alumina Al_2O_3 together with potash, soda, and portland cement. The flotation agents in this process are oleic acid (275 g/t) and kerosene (up to 500 g/t).

Flotation of Coals. Coals contain trace amounts of FeS_2 and SiO_2. To obtain high-quality metallurgical coke and to minimize the H_2S content in the coke-oven gas, coals of various grades are dressed with a view to removing FeS_2 and SiO_2. The flotation agents used in this process are kerosene (500 g per tonne of coal) or pine oil (75 g per tonne of coal).

Flotation of Sulphide Ores. Sulphide ores containing 1.5 to 2.0% of copper serve as a compound source of sulphuric acid and copper. Copper is present in sulphide ores in the form of $CuFeS_2$, Cu_2S and CuS. Flotation is done to increase the copper content in the ore
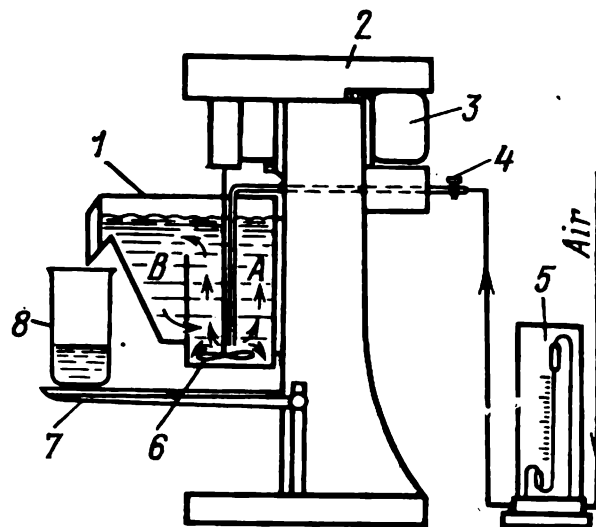
and to obtain pyrite in the form of tailings, used as a source of sulphuric acid. The flotation agents include pine oil or creosol (25-75 g/t) and potassium xanthate (100 g/t).

Flotation of Baltic Shales. Shales occupy an intermediate position between solid and liquid fuels in terms of composition of the combustible matter. Its organic part contains 75% of carbon, 10% of hydrogen, and 15% of oxygen. The incombustible part contains water and such mineral ingredients as carbonates, phosphates and sulphates of iron, calcium, magnesium, and other metals. When shale is burnt, these substances remain in the form of ash which accounts for 30 to 60% of the shale weight.

The low-temperature carbonization of shales yields approximately up to 35% of tar, 56% of low-temperature coke, and 1.5% of water. The yield of gas is 70 m^3/t. Shale tar is a source of motor fuels and other valuable organic products.

The flotation of shales is intended to increase the content of the combustible portion, hence, the tar yield in low-temperature carbonization. The flotation agents in this case are as follows: collector—shale tar (200-300°C fraction—500 g per tonne of shale), and frother—pine oil (200 g per tonne of shale).

After the flotation experiment, the results are tabulated in the following manner:

Ore weight before flotation, g	After flotation			Weight of concentrate, %	Losses, %
	concentrate weight, g	weight of tailings, g	total weight, g		

The starting ore and the samples of concentrates and tailings, taken after flotation, can be analyzed for content of the desired component (see Laboratory Works "Low-Temperature Carbonization" and "The Kinetics of Sulphide Ore Roasting").

LITERATURE

Glembotsky, V. A. and Klassen, V. I., *Flotation*, Moscow, 1973.

Instructions to the Laboratory Work "Flotation"

1. Place the weighed amount of ore in the agitation compartment of the flotation cell.
2. Pour water on the charge so that the pulp level is below the partition between the cell compartments.
3. Add the necessary flotation agents in the specified amount.
4. Activate the mechanical and pneumatic agitation; preset the air flow rate by means of the restrictor valve and rheometer.
5. Switch on the froth skimmer.

6. After the experiment, switch off the froth skimmer, stop **the** agitation, and remove the tailings from the cell.
7. Clean the air feed ports clogged with the floated material.
8. Wash the cell with water, with the motor running.
9. Do not operate the flotation cell with the drive guard removed.
10. Do not carry out any repair on the operating cell.

LABORATORY WORK 30. WATER TREATMENT

The extent to which water is used in various chemical processes is quite impressive. It performs the function of a universal solvent for a host of solid, liquid and gaseous substances. Water is also important as a starting substance in the production of hydrogen, sulphuric and nitric acids, sodium hydroxide, lime, as well as in various reactions of hydration and hydrolysis. Apart from being employed as a process agent, enormous quantities of water are used for heat transfer and cooling. It is used, for example, to remove heat from the reaction zone in exothermic processes. Steam and heated (or superheated) water are used to supply heat in endothermic processes for raising the temperature of the reagents and, thereby, speeding up many processes.

The heat transfer between reagents and water is effected in heat exchangers, coolers, and heaters of various types. The heat is transferred to water from liquid or gaseous reagents through the wall of these devices or, less frequently, with direct contact between water and the reagents. Water consumption at large plants amounts to millions of cubic metres per day. Part of the water (primarily that used for heat transfer purposes) is returned into the system after cooling and cleaning (recycled water).

Since water is a good solvent, raw water normally contains various impurities. The water used at chemical and power plants must meet stringent requirements as regards the content of dissolved matter, suspended solids, microorganisms, and so on.

Depending on the application of water, its physical, chemical and bacteriological characteristics must comply with certain requirements: domestic and potable water must be harmless for health and meet appropriate standards concerning its odour, taste, colour, clearity, hardness, content of lead, arsenic, iron, and so forth (State Standards GOST 2919-45 and GOST 4152-72).

The water to be used as a coolant must have limited contents of salts (Ca, Mg), iron, suspended solids, and be absolutely free of hydrogen sulphide. The water for steam power facilities must contain a minimum of salts, alkalis, greases, oil, and silicic acid.

As far as process water is concerned, the requirements it must meet are imposed by each particular process.

Before water is supplied to a plant, it must be treated according to the impurities it contains and process requirements. Process wa-

ter must be free of substances detrimental for the reaction involved; it must not corrode the equipment and form scale and sludge in apparatus and piping. Impurities are usually present in water in the form of solutions, colloids, or suspended solids. The basic operations involved in water treatment include removal of suspended solids, softening, and, in some cases, neutralization, demineralization, deaeration, degassing, and disinfection. For removal of suspended solids, water is allowed to settle or filtered through a sand or gravel bed. The clarification of water, or coagulation of colloidal impurities, is carried out by addition of coagulants, such as $Al_2(SO_4)_3$, $FeSO_4$, and $NaAlO_2$, or flocculants (promoters of flake formation), such as colloidal silicic acid, natural and synthetic polymers. The coagulating action of one of the most commonly used coagulants, $Al_2(SO_4)_3$, is based on formation of aluminium hydroxide as a result of interaction with the bicarbonates present in the water being purified:

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 3CaSO_4 + 2Al(OH)_3 + 6CO_2$$
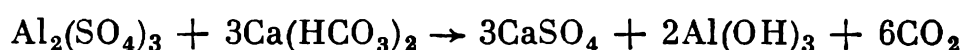
If water contains no dissolved bicarbonates, lime is added expressly to shift the equilibrium of the $Al_2(SO_4)_3$ hydrolysis reaction toward formation of $Al(OH)_3$ molecules possessing a high positive charge, which promotes the coagulation of particles. In this case, the particles of colloidal impurities become enlarged as a consequence of aggregation (agglutination) of aluminium hydroxide and precipitated, together with organic impurities and bacteria by flocs. After the precipitate has settled, it undergoes filtration.

One of the major factors determining the quality of water is its hardness dependent on the content of the magnesium and calcium salts dissolved in it. The water hardness may be temporary, permanent, and total.

The *temporary (carbonate) hardness* is characterized by the presence in water of dissolved bicarbonates $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$, which change to neutral or basic salts during boiling and precipitate

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

$$2Mg(HCO_3)_2 \rightarrow MgCO_3 \cdot Mg(OH)_2 + 3CO_2 + H_2O$$
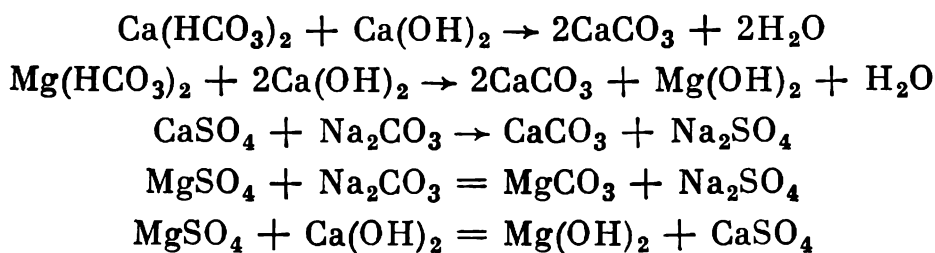
The *permanent hardness* is due to the presence of magnesium and calcium nitrates, chlorides, and sulphates, which do not precipitate during boiling.

The *total hardness* is the sum of temporary and permanent hardnesses. Raw water is classified as follows, in terms of hardness which is defined by the content of Ca^{2+} and Mg^{2+} (mg. eq.) in a cubic decimetre of water:

very soft 0-1.5

soft 1.5-3

moderately hard 3-6

hard 6-10

very hard 10

Water softening implies complete or partial removal of calcium and magnesium salts. Coarse softening (approximately to 0.3 mg. eq./dm^3) is achieved by addition of lime and sodium hydroxide, or soda (lime-soda process):

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + H_2O$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

$$MgSO_4 + Na_2CO_3 = MgCO_3 + Na_2SO_4$$

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$$

and so on.

The carbon dioxide dissolved in water reacts with slaked lime:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
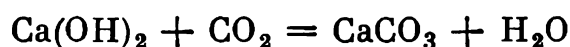
When trisodium phosphate Na_3PO_4 is used as the softener eliminating both temporary and permanent hardness, the softening is more complete (down to 0.03 mg. eq./dm^3).

Raw water with low hardness or after coarse softening can most effectively be softened in the ion-exchange process as well. This process resides in that some solid poorly soluble mineral and organic substances are capable of extracting some cations or anions from the solution in exchange for others present in them. To extract Ca^{2+}, Mg^{2+} and Fe^{3+} ions from water, use is made of cation exchangers, such as sulphonated coal or high-molecular resins containing active groups with H^+, Na^+ or NH_4^+ ions. Cation-exchange processes can be represented as

$$2(Cat)H + Ca(HCO_3)_2 \rightarrow (Cat)_2Ca + 2CO_2 + 2H_2O$$

$$2(Cat)Na + CaSO_4 \rightarrow (Cat)_2Ca + Na_2SO_4$$

$$2(Cat)Na + Mg(HCO_3)_2 \rightarrow (Cat)_2Mg + 2NaHCO_3$$

as well as

$$(Cat)H + NaCl \rightarrow (Cat)Na + HCl, \text{ and so on.}$$
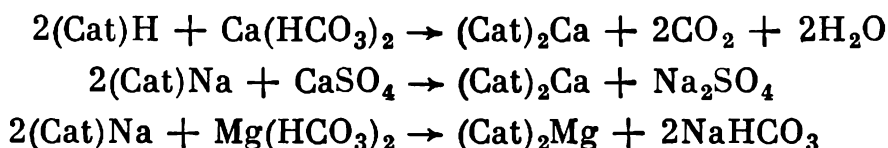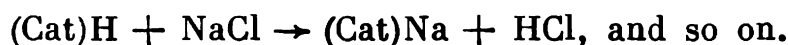
For water to be completely demineralized (deionized) downstream of the cation exchanger, it is passed through an anion exchanger:

$$(An)OH + HCl \rightarrow (An)Cl + H_2O$$

$$2(An)OH + H_2SO_4 \rightarrow (An)_2SO_4 + 2H_2O$$
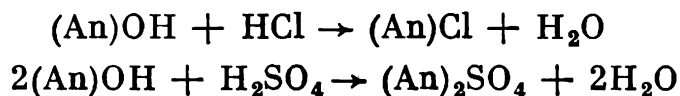
The cation and anion exchangers are regenerated by treatment with
alkaline, acid or sodium chloride solutions, for example:

$$(Cat)_2Ca + 2NaCl \rightarrow 2(Cat)Na + CaCl_2$$

$$(Cat)_2Ca + 2HCl \rightarrow 2(Cat)H + CaCl_2$$

$$(Cat)_2Mg + H_2SO_4 \rightarrow 2(Cat)H + MgSO_4$$

$$(An)Cl + NaOH \rightarrow (An)OH + NaCl$$

By mixing the grains of the cation and anion exchangers, one can
extract both cations and anions from water. As anion exchangers
are used resins resulting from interaction between amines and for-
maldehyde or between polyethylene polyamines and epichlorohydrin.

The *disinfection* of water is achieved by using chlorine or chlori-
nated lime and, less commonly, ozone.

Deaeration or *degassing* implies removal of oxygen and carbon
dioxide, dissolved in water and attacking boiler steel; CO_2 is absorbed
by $Ca(OH)_2$, while oxygen is fixed by means of iron filings or shavings.

Up-to-date processes of water treatment are developed on the
basis of the contaminant classification offered by the Academy of
Sciences of the Ukrainian SSR. All contaminants of raw and pro-
cess water can be divided into four groups, the contaminants of
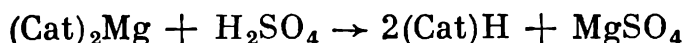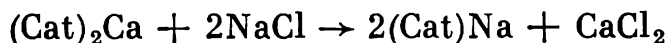each group exhibiting specific properties and calling for particular
techniques of their removal. Knowing the properties of these groups,
one can select an appropriate combination of effective treatment
techniques for each, enabling the phase-dispersion state of water
contaminants to be varied to achieve the desired results.

This work covers the basic water treatment processes and stan-
dard methods for determining the water hardness.

Experimental Procedure

Lime-Soda Process. First, the carbonates, non-carbonate and mag-
nesia hardness of water are determined along with the carbon dioxide
content. The results are used to calculate the amounts of lime and
soda, necessary to soften the water. It has been established, for
example, that the carbonate hardness is 6 mg.eq./dm³, the non-carbo-
nate one is 2 mg.eq./dm³, the magnesia hardness is 3 mg.eq./dm³,
and the carbon dioxide content is 9 mg/dm³.

Required for water softening are

Ca(OH)₂

$$6 + 3 + 9^1/_{22} = 9.4 \text{ mg.eq./dm}^3,$$

where 1/22 is the factor of conversion of CO_2 to mg.eq./dm³, either
$9.4 \cdot 74/2 = 347.8$ mg/dm³ or 0.348 g per dm³ of water,

Na₂CO₃

$$2\frac{106}{2} = 106 \text{ mg/dm}^3 = 0.106 \text{ g per dm}^3 \text{ of water.}$$

The calculated amounts of lime and soda are metered to within 0.01 g and dissolved in one litre of the water being softened. The contents of the flask are shaken for 3 to 5 min, allowed to stand, and filtered through a folded filter. The first portions of the filtrate are thrown away. After 200 cm³ of the filtrate have been taken aside, the three hardnesses and the content of dissolved carbon dioxide are determined.

Ion-Exchange Process. The cation-exchange apparatus is essentially a glass tube *1* (Fig. 103) 60 to 80 cm long and 2.5 to 3.5 cm in diameter, with a glass perforated plate *3* sealed into its lower portion. The tube terminates in a discharge cock *4* and is filled with a cation exchanger *2* (sulphonated coal or some other substance) so that the pile it forms in the tube is 40 to 50 cm high. To regenerate the cation exchanger and saturate it with Na⁺ ions, 700 cm³ of a 6-8% sodium salt solution are passed through the column at such a rate that it takes 25 to 30 min for the brine to flow through the cation exchanger. Then, the regenerated cation exchanger is washed with water to remove the excess NaCl till the Cl⁻ ions disappear completely (silver nitrate test), which requires approximately 1000 cm³ of water. After the cation exchanger has been washed, 200 to 250 cm³ of the water being softened are passed through the filter at a prescribed rate adjusted by the cock *4*. The total hardness is then determined both in the filtered (softened) water and in the raw water.
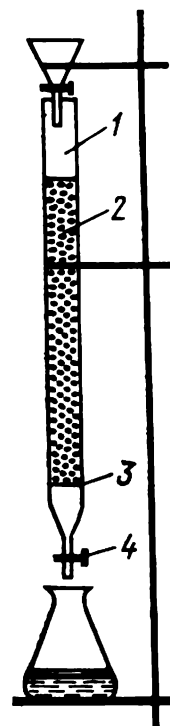
Fig. 103. Cation-exchange apparatus

The *total water hardness* can be determined (a) chelatometrically, involving titration with a Trilon B solution in the presence of chromogen indigo or black in an ammonia medium (pH 9-10); or (b) gravimetrically and volumetrically from the calcium and magnesium contents in water.

The chelatometric method of determining the total water hardness is based on the fact the calcium and magnesium ions are bound by Trilon B into complex compounds. The reactions involved are as follows:

$$Ca^{2+} \quad \begin{matrix} Na-OOC-CH_2 \\ H-OOC-CH_2 \end{matrix} \Big\rangle N-CH_2-CH_2-N-\Big\langle \begin{matrix} CH_2COONa \\ CH_2COOH \end{matrix} =$$

$$= \left[\begin{matrix} OOC-CH_2 \\ OOC-CH_2 \end{matrix} \Big\rangle N \Big\langle \overset{Ca}{\underset{(CH_2)_2}{\cdots}} \Big\rangle N \Big\langle \begin{matrix} CH_2COO \\ CH_2COO \end{matrix} \right] Na_2 + 2H^+$$

and
<center>Trilon B</center>

$$Mg^{2+} + \begin{matrix} Na-OOC-CH_2 \\ \diagup \\ H-OOC-CH_2 \end{matrix} N(CH_2)_2-N \begin{matrix} CH_2COONa \\ \diagup \\ CH_2COOH \end{matrix} =$$

$$= \left[\begin{matrix} OOC-CH_2 \\ \diagup \\ OOC-CH_2 \end{matrix} N \begin{matrix} Mg \\ \diagdown \\ (CH_2)_2 \end{matrix} N \begin{matrix} CH_2COO \\ \diagdown \\ CH_2COO \end{matrix} \right] Na_2 + 2H^+$$
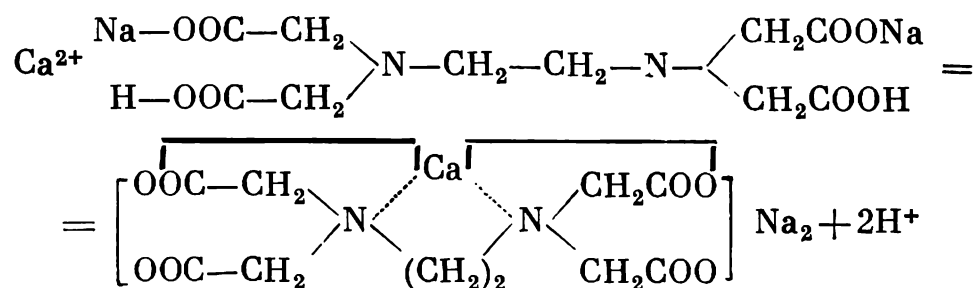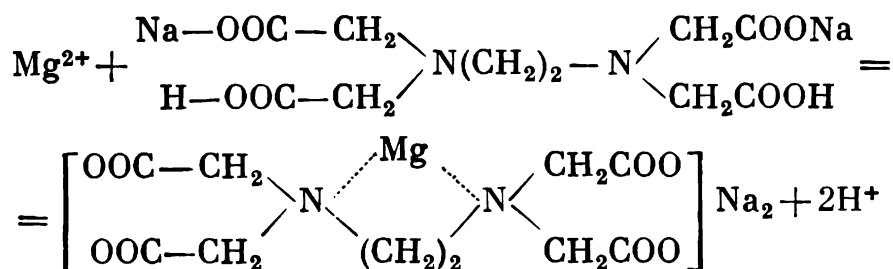
The end of the reaction is marked by the chromogen black indicator changing its colour from pink-crimson to bluish black. The appearance of a bluish gray colour is indicative of the absence of Ca^{2+} and Mg^{2+} ions in the solution, that is of their complete binding by Trilon B.

Prior to analysis, 100 to 150 cm³ of the water under investigation are poured into a 250-cm³ conical flask, to which are added 5 cm³ of the ammonia buffer and 6 to 7 drops of the chromogen indicator, and the solution is slowly titrated with a 0.05-0.1 N solution of Trilon B till the colouration changes from red to bluish gray (violet). The total water hardness H_{total} (mg.eq./dm³) is calculated using the formula

$$H_{total} = v_1 k 1000/v, \tag{5.1}$$

where v_1 is the amount of 0.1 N solution of Trilon B, spent in the titration of the sample, in cm³; k is the normality factor of the Trilon B solution, $k = H_{act}/0.1\ N$; and v is the water sample volume, in cm³.

For gravimetric and volumetric determination of the calcium and magnesium contents in water, the calcium ion is precipitated in the form of calcium oxalate:

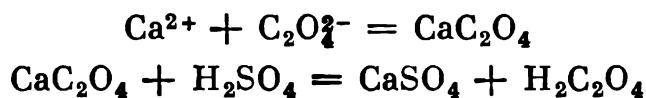$$Ca^{2+} + C_2O_4^{2-} = CaC_2O_4$$
$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4$$

The resulting oxalic acid is titrated with potassium permanganate:

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

To 100 cm³ of the analyzed water HCl is added till the litmus shows an acid reaction. The solution is heated to boiling, 10 cm³ of 10% NH_4CL are added first, then 15 cm³ of an $(NH_4)_2C_2O_4$ solution with stirring. Three to four drops of ammonia are added 10 to 15 minutes later till it produces a slight odour. The solution with the precipitate are allowed to stay on a water bath for 10 to 15 min. The calcium oxalate precipitate is filtered and washed with an ammonia oxalate solution. The washed precipitate is dissolved on a filter with sulphuric acid, the filtrate is heated to boiling and titrated with potassium permanganate till appearance of pink colour. The Ca^{2+} ion concentration (mg/dm³) is calculated from the formula

$$C_{Ca^{2+}} = T_{KMnO_4} v \frac{1000 \cdot 100}{100}, \tag{5.2}$$

where T_{KMnO_4} is the titre of $KMnO_4$ in terms of the Ca^{2+} ion, and v is the amount of $KMnO_4$, spent in the titration.

Magnesium is determined by volumetric analysis. To this end, the bicarbonates and carbonates present in the water are converted to chlorides by titration with hydrochloric acid. The resulting carbon dioxide is removed by boiling. Magnesium is precipitated with excess $Ca(OH)_2$:

$$Mg^{2+} + Ca(OH)_2 = \downarrow Mg(OH)_2 + Ca^{2+},$$
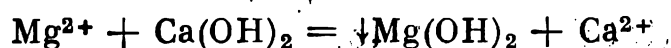
The precipitate is filtered, and the excess calcium oxide is titrated with 0.1 N HCl.

To carry out the analysis, to 100 cm³ of water are added three drops of methyl orange, followed by titration with 0.1 N HCl till appearance of orange colour; also titrated is a blank assay containing 100 cm³ of distilled water. Both flasks with solutions are heated to boiling, the contents are transferred into 200-cm³ measuring flasks, 50 cm³ of a saturated $Ca(OH)_2$ solution are added to each flask, and water is added to make up the solutions to the lower edge of the flask neck. The contents of the flasks are stirred, and the flasks are put on a water bath for half an hour. After cooling, the contents are made up to the mark, stirred, and the magnesium hydroxide precipitate is filtered. From each sample 100 cm³ of the filtrate are titrated with 0.1 N HCl in the presence of phenolphthalein, with the excess calcium hydroxide being bound. The amount of magnesium is calculated from the formula

$$C_{Mg^{2+}} = \frac{12.16 \cdot 2\,(Nv_1 - Nv_2)\,1000}{100}, \tag{5.3}$$

where 12.16 is g.eq. of magnesium; N is the normality of hydrochloric acid; v_1 is the amount of hydrochloric acid, spent in the titration of the blank assay, in cm³; and v_2 is the amount of hydrochloric acid, spent in the titration of the water sample, in cm³. The total water hardness (mg.eq./dm³) is determined from the formula

$$H_{total} = \frac{C_{Ca^{2+}}}{20.04} + \frac{C_{Mg^{2+}}}{12.16}, \tag{5.4}$$

$C_{Ca^{2+}}$ and $C_{Mg^{2+}}$ being the concentrations of Ca^{2+} and Mg^{2+} ions, in mg.eq./dm³.

Carbonate Hardness. We titrate 100 cm³ of the analyzed water with 0.1 N HCl in the presence of methyl orange till appearance of pink colour. The carbonate hardness (mg.eq./dm³) is calculated using the formula

$$H_{carb} = \frac{Nv_1}{v_2}\,1000, \tag{5.5}$$

where N is the normality of HCl; v_1 is the amount of HCl, spent in the titration, in cm³; and v_2 is the water sample volume, in cm³.

Non-Carbonate Hardness. The non-carbonate hardness is determined from the difference between the total and carbonate hardnesses:

$$H_{non\text{-}carb} = H_{total} - H_{carb}. \qquad (5.6)$$

The efficiency of the water softening procedures is characterized by the degree of water softening η_{soft}, defined as the ratio of the water hardness (total, carbonate, non-carbonate) after softening to that before softening:

$$\eta_{soft.total} = \frac{H_{total.soft.}}{H_{total.raw}}$$

or

$$\eta_{soft.carb.} = \frac{H_{carb.soft.}}{H_{carb.raw}} \quad \text{and}$$

$$\eta_{soft.non\text{-}carb.} = \frac{H_{non\text{-}carb.soft.}}{H_{non\text{-}carb.raw}},$$

where $\eta_{soft.total}$, $\eta_{soft.carb.}$, and $\eta_{soft.non\text{-}carb.}$ are the degrees of softening with respect to total, carbonate and non-carbonate hardnesses, respectively.

To determine the *carbon dioxide content*, 200 cm³ of the analyzed water is poured into a round-bottomed flask, 0.2 cm³ of a 1% phenolphthalein solution is added, and the whole is stirred. If the colour of the water becomes more intense in comparison with that of the reference solution, the water is free of dissolved carbon dioxide. Lack of colouration or a paler colour attests to the contrary. In this case, the sample is titrated with 0.1 N NaOH till the reference solution acquires some colouration.

The carbon dioxide content is determined from the formula

$$C_{CO_2} = 44Nv1000/200, \qquad (5.7)$$

where N is the normality of NaOH, and v is the amount of NaOH, spent in the titration, in cm³.

LITERATURE

Klyuchnikov, N. G., *A Practical Course in Chemical Technology*, 3rd revised and expanded edition, Moscow, 1972.
Kulsky, L. A. and Dal., V. V., *Problems of Pure Water*, Kiev, 1974.
Kulsky, L. A. *The Basic Theory of Water Treatment*, Kiev, 1968.

Instructions to the Laboratory Work "Water Treatment"

A. Lime-Soda Process

1. Determine the carbonate, non-carbonate and magnesia hardnesses of water and the carbon dioxide content in it.
2. Calculate the necessary amount of lime and soda.

3. Weigh the calculated amounts of lime and soda, dissolve them in one litre of the water to be softened, shake the solution, and allow it to settle.
4. Filter the settled water.
5. Throw away the first portions of the filtrate.
6. Take 200 cm³ of the filtrate for analysis according to the assignment.
B. **Ion-Exchange Process**
1. Regenerate the cation exchanger in the cation-exchange apparatus by passing a sodium salt solution through the column.
2. Wash the cation exchanger with water to remove the excess salt.
3. Soften water by passing it through the cation-exchange column at a predetermined rate.
4. Analyze the raw and softened water according to the assignment.
5. Take the necessary precautions when handling acids. While diluting sulphuric acid, pour it into water. When working with hot solutions and boiling water bath, be careful about burns.

LABORATORY WORK 31. DETERMINATION OF DISPERSITY, DENSITY OF SOLID LOOSE MATERIALS, DENSITY AND VISCOSITY OF LIQUIDS

A. **Solid and Loose Materials.** These are widely employed in the chemical industry as raw materials, reaction products, and catalysts of chemical reactions. The basic technical and process characteristics of solid materials, to a great extent determining their properties and quality, include dispersity (granulometric composition), density (true, apparent, and bulk), porous structure, specific surface, and others. When such characteristics are not available, it is impossible, in some cases, to determine the necessary process parameters, to attain a sufficiently high product yield, to ensure the desired properties of the products, and so on.

This work has to do with determination of some physical characteristics of solid loose materials.

Sieve Analysis. The sieve analysis is intended to determine the dispersity of powdered materials while monitoring industrial processes as well as in various scientific, laboratory and production tests; sieves are also used when a material has to be separated into fractions with grains of a particular size.

This analysis uses standard metal sieves (less often, silk or synthetic) or series of round- and square-mesh sieves. Sieves are normally designated by the sieve size or number of meshes per square centimetre, number of meshes per centimetre, and so on. The State Standard GOST 35-84-53, currently in force, includes the sieve scale characteristics (Table 15). The sieve screens are made of brass, phosphor bronze, stainless and low-carbon steels.

It should be remembered that the average grain size of a material is always slightly smaller than that derived from the sieve analysis data, because in most cases grains are irregular in shape.

To determine the fineness of grinding of fine-grained materials, a weighed amount of a predried material (50 to 100 g) is poured on a

sieve fitted in a tray; after the sieve has been covered by a lid, the sample is sifted by shaking the sieve assembly in a tilted position and gradually turning it through 360° about the vertical axis. At the end of the experiment, the sample is sifted over a sheet of paper,

Table 15

Sieve size	Sieve opening, mm	Wire diameter, mm	Number of meshes per cm² of the screen	Percentage free area
2.5	2.5	0.5	11.2	70
2	2.0	0.5	16.0	64
1	1.0	0.35	54.9	55
0.5	0.5	0.22	193	48.2
0.25	0.25	0.13	694	43.3
0.1	0.1	0.07	3,460	34.6
0.05	0.05	0.035	13,900	31.0

without the tray. The sifting is considered to be over if not more than 0.1% of the material passes through the sieve within a minute. The fineness of grinding is expressed as percentage, after weighing the material remaining on the sieve.
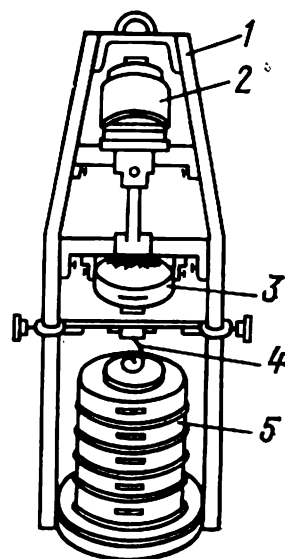
Fig. 104. Vibrating screen

To determine the granulometric composition of a material, a series of sieves is used, including a different number of sieves depending on the required number of fractions. The sieves are stacked between the lid and the tray so that the sieve with the finest mesh is the lowermost, while that with the coarsest mesh is the uppermost. A weighed amount of a dry material (up to 1 kg) is poured on the top sieve, the lid is placed, and the sample is sifted manually or mechanically.

Figure 104 represents one of the most common types of sieves, known as the vibrating screen. On the frame *1* is secured an electric motor *2* arranged vertically with a vibrator *3*. The stack of sieves *5* is held in place by means of a spring *4*. The frame is freely suspended. When the motor is energized, the entire system starts vibrating at a frequency equal to the rotational speed of the motor. Also used for the purpose may be sieves arranged in a stack adapted to reciprocate and secured on a shaker. The screening time is about 20 min. After screening, the material remaining on the different sieves is weighed, and the granulometric composition is calculated.

Example of Calculation. After screening of 500 g of a granular material, the followtng size grading has been obtained:

Sieve size	Average particle size, mm	Material remaining on sieve, g	Weight percentage of the total
5	> 5	23	4.6
3	$\dfrac{-5+3}{2} = 4$	172	34.4
2	$\dfrac{-3+2}{2} = 2.5$	201	40.2
1	$\dfrac{-2+1}{2} = 1.5$	12	2.4
05	$\dfrac{-1+0.5}{2} = 0.75$	47	9.4
025	$\dfrac{-0.5+0.25}{2} = 0.38$	5	1.0
	< 0.25	40	8.0

The weight ratio of the material remaining on the sieve to the total sample represents the percentage content of a given average fraction in the total volume. For example, the particles with an average size of 4 mm account for $\dfrac{172}{500} 100 =$ $= 34.4\%$.

Determination of Density. Most granular solids are characterized by porous structure, that is the presence in granules of ducts and voids differing in size and shape, whereby the inner surface of the granules varies widely. Depending on the porous structure, shape and size of particles, the granular material has different densities per unit volume. Distinction is made between true, apparent and bulk densities.

Determination of True Density. By true density is meant the mass of a given solid per unit volume, minus the pore volume. Of all the known ways to determine true density, the most widely used is the pycnometric method. Pycnometers are nothing but graduated vessels having a capacity of 1 to 100 cm³ and various shapes, whose exact volume can be determined by weighing with water.

To determine the true density of a solid material, a washed and dried pycnometer is filled with a pycnometric liquid*, and its temperature is maintained at 20 ± 0.2°C by means of a thermostat for 30 min. Then, the liquid level in the graduated pycnometer is checked, the inner surface of the pycnometer above the level mark is care-

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* The picnometric liquid may be any organic substance, such as petrol, kerosene, benzene, toluene, ethanol, as well as water and other liquids in which the solid particles do not dissolve.

fully wiped with filter paper, the pycnometer is stoppered and weighed on an analytical balance. After that, the pycnometer is emptied, dried and weighed together with the stopper. A material sample is charged through a funnel in an amount sufficient for the pycnometer bottom to be covered by a layer one or two grains thick. The pycnometer is stoppered and weighed to determine the amount of the sample. The 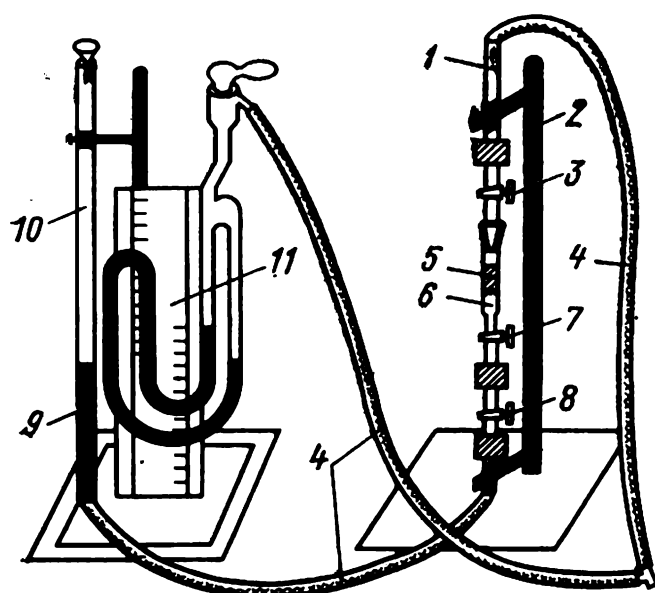pycnometric liquid is then poured on the sample (up to half the height of the wider portion of the pycnometer), the unstoppered pycnometer is placed in the thermostat at 80 to 90°C and held there for about an hour, making sure that the sample is always covered by the liquid. While the liquid is boiling, the air filling the pores of the sample is replaced by the liquid.

Air can also be expelled from a powdered material by holding an unstoppered pycnometer under vacuum in an exiccator (the exiccator is evacuated by a water-jet pump). The pycnometer is then withdrawn from the thermostat, cooled, liquid is added up to the mark, the stopper is placed, and the temperature in the thermostat with the pycnometer is maintained at 20 ± 2°C for 30 min. The liquid is removed from the wall above the mark, the pycnometer is stoppered and weighed again on the analytical balance. The true density of the solid material is calculated using the formula

Fig. 105. Instrument for determining apparent density

1—adapter tube; *2*—upright; *3*—cock; *4*—vacuum hoses; *5*—graduated container with ground-glass joints; *6*—sample; *7*, *8*—cocks; *9*—mercury; *10*—mercury burette; *11*—vacuum gauge

$$\rho_{true} = \frac{\rho_1 g}{M_1 - (M_2 - g)} , \qquad (5.8)$$

where ρ_{true} is the true density of the solid material, in g/cm^3; ρ_1 is the density of the pycnometric liquid at 20°C, in g/cm^3; g is the sample weight, in g; M_1 is the mass of the pycnometer with the liquid, in g; and M_2 is the mass of the pycnometer with the liquid, and sample, in g.

Determination of Apparent Density. The mass per unit volume of a granular material, including the volume of its pores, is known as apparent density. The setup for determining apparent density is illustrated in Fig. 105. The density is determined in a graduated container *5* which is weighed on an analytical balance, then filled with a sample of the granular material up to the stopper. The con-

tainer with the sample is weighed again. Next, the container is connected to a roughing-down pump through a tube *1* and a vacuum hose *4*; with the cocks *3* and *7* open and the cock *8* closed, air is pumped from the container, sample, and hoses till the mercury level in both legs of the vacuum gauge *11* becomes the same. The evacuation takes two or three minutes. Then, without stopping the evacuation, the cock *8* is carefully opened, and the container with the tube *1* above it are filled with mercury to a height of 80-100 mm, which creates positive pressure over [the sample and provides for more complete filling of the intergranular space with the mercury. The cocks *7* and *8* are then closed, the hose is carefully removed from the upper end of the tube *1*, and the roughing-down pump is switched off. The mercury additionally fills the voids between grains at atmospheric pressure and, if the material is porous, partially fills the larger pores. The cock *3* is closed, the mercury from the tube *1* is transferred into a burette *10*, the open ends of the container are thoroughly cleaned of mercury, and the container with the sample and mercury is weighed on the analytical balance.

Fig. 106. Device for determining bulk density

The mass of the container with mercury but without the sample is determined in a similar manner.

The apparent density ρ_{app} is calculated from the formula

$$\rho_{app} = \frac{13.59g}{M_1 - (M_2 - g)} , \qquad (5.9)$$

where g is the sample weight, in g, M_1 is the mass of the container with mercury, in g; M_2 is the mass of the container with mercury and the sample, in g; and 13.59 is the density of mercury, in g/cm^3.

Determination of Bulk Density. Bulk density is defined as the mass per unit volume of a loose material in its natural state, with due account for its porosity*. It can be determined in the loose or compacted state. Bulk density in the loose state is determined with the aid of a funnel-shaped device (Fig. 106). It comprises a truncated cone *1* terminating in a tube *2* with a gate *3* at its end. The funnel is held at a particular height by an upright *4*. Under the tube of the cone is placed a measuring vessel *5* (0.1 to 1.0 dm^3). The funnel with the gate closed is charged with the material in an amount equal to twice the volume of the vessel *5*. The gate is opened, and the vessel *5* is filled with the material to overrunning. The gate is shut, and the

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* By porosity is meant the amount of free space in a granular material layer.

excess material is skimmed by a metal or wooden rule held obliquely against the rim of the vessel 5. Then, the vessel is weighed with and without the material.

The bulk density is determined from the formula

$$\rho_{bulk} = \frac{M_1 - M_2}{v}, \tag{5.10}$$

where ρ_{bulk} is bulk density, in g/cm³; M_1 is the mass of the vessel with the material, in g; M_2 is the mass of the empty vessel, in g; and v is the vessel volume, in cm³.

The determination is carried out three times, and the arithmetic mean of the three results is taken.

Bulk density in the compacted state is determined as follows: the material charged into the measuring vessel in portions is compacted by tapping the vessel against a solid surface to a constant volume. The determination is also carried out three times.

B. Liquids. Liquid reagents, reaction products, heat-transfer agents, coolants, and catalysts are extensively used in the chemical industry. These are solutions of gaseous, liquid and solid substances in water and other solvents, liquid-phase organic and inorganic compounds, emulsions, suspensions, multicomponent systems, such as petroleum and products of its refining, and so on. The basic physical parameters characterizing the properties of liquids are density and viscosity.

Determination of Liquid Density. The density ρ of a liquid (g/cm³) is defined by the mass of the substance per unit volume

$$\rho = G/v. \tag{5.11}$$

The relative density d is the ratio between the densities of two substances under particular standard conditions, the second substance usually being distilled water:

$$d = \rho/\rho_w. \tag{5.12}$$

If the volumes of the test substance and water are equal, the density is expressed as the ratio of their masses:

$$d = G/G_w. \tag{5.13}$$

At present, relative density is usually defined as the ratio between the density of the test substance at normal temperature (20°C) and that of distilled water at 4°C and designated d_4^{20}.

In view of the temperature dependence of the liquid density, it is always necessary to indicate the temperature at which the density was measured and introduce correction factors.

The thermal coefficient β of volume expansion represents the change in volume, occurring when the temperature is varied by 1°C.

Table 16 lists the coefficients β of thermal expansion of some liquids within a particular temperature range

Table 16

Liquid	β, 1/°C	Temperature range, °C
Petrol	0.00124	10-30
Water	0.00020	10-30
Glycerine	0.00050	15-30
Kerosene	0.00090	0-100
Ethanol	0.0011	0-40

To convert the density measured at a temperature t to that measured at $t = 20°C$, one can use the relation proposed by D. I. Mendeleev:

$$d_4^{20} = d_4^t + \alpha\ (t - 20). \tag{5.14}$$

As can be inferred from Eq. (5.14), the density of liquids decreases with increasing temperature. Table 17 lists the mean correction factors to the density of petroleum products.

Table 17

Density, g/cm³	Temperature correction factor, g/(cm³·°C)	Density, g/cm³	Temperature correction factor, g/(cm³·°C)
0.6900-0.6999	0.000910	0.8500-0.8599	0.000699
0.7200-0.7299	0.000870	0.9000-0.9099	0.000633
0.7500-0.7599	0.000831	0.9500-0.9599	0.000567
0.8000-0.8099	0.000765	0.9900-1.0000	0.000515

The basic methods for measuring the density of liquids include the simplest hydrometric method and the most accurate (most time-consuming) pycnometric method.

Hydrometric Method. The instruments for measuring the density of liquids, or hydrometers, are divided into two groups: (1) hydrometers (densitometers) with a scale graduated in density units, and (2) hydrometers for measuring the concentration of a solution graduated in volume or weight per cent.

Densitometers are further classified depending on whether they are used to measure the density of liquids lighter or heavier than water: oil hydrometers, lactometers, densitometers for storage batteries, and so on. The hydrometers of the second group include alcoholometers, saccharimeters, glue and other hydrometers.

A glass hydrometer (Fig. 107) consists of a hollow cylindrical or fusiform bulb with a cylindrical thin-walled neck with a sealed end extending upward from the bulb. The bottom portion of the hydrometer is filled with a ballast for stability when the hydrometer is immersed in the liquid. To the inner surface of the neck is attached a calibrated scale. Some hydrometer types (oil hydrometer, etc.) are made with a built-in thermometer, which permits temperature to be measured simultaneously with density (concentration). To determine the density of a liquid or concentration of a solution, one must first of all select an appropriate hydrometer and its measurement range.

The liquid to be measured is poured into a glass cylinder whose internal diameter is at least twice as long as the outer diameter of the hydrometer and which is slightly higher than the hydrometer. The difference between the liquid and ambient temperatures must not exceed $\pm 5\%$.

A clean dry hydrometer held by the upper tip is immersed into the cylinder with the test liquid. After the hydrometer stops vibrating and settles, a measurement is taken with reference to the upper edge of the meniscus (the eye must be level with the meniscus). At the same time, the liquid temperature is measured. The reading on the hydrometer scale corresponds to the liquid density at the test temperature. To reduce this density to d_4^{20} (at 20°C), Eq. (5.14) is used.

(a)   *(b)*   *(c)*
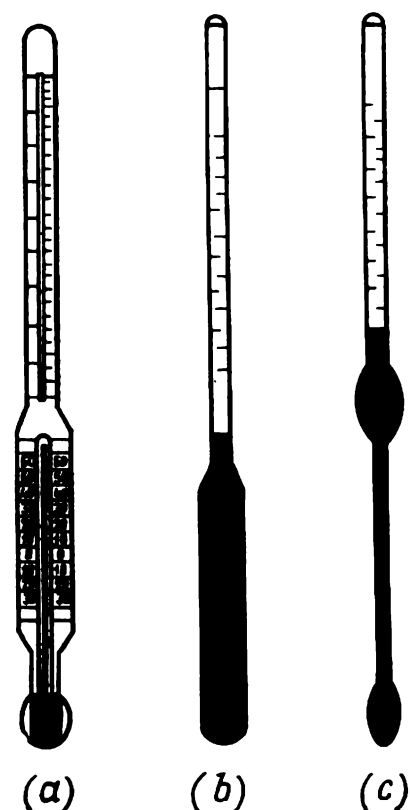
Fig. 107. Hydrometers
a—oil hydrometer; b, c—general-purpose hydrometers

Pycnometric Method. This is one of the most accurate methods (to within 0.002 g) and permits measurements even at very low concentrations of the product (1-2 cm³). The method is based on variations in the mass of a liquid taken within a definite volume, related to the mass of water of the same volume and at the same temperature.

The density of a wide variety of liquids can be measured by a pycnometer. The most common are the following instruments: U-tube pycnometer having a capacity of about 1 cm³ (Fig. 108a), long-neck pycnometer (Fig. 108b), and plug-type pycnometer (Fig. 108c). The latter two are adopted as standard pycnometers; their capacity for measuring the density of petroleum products is, according to State Standard GOST 3900-47, 5.0, 10.0, or 25.0 cm³.

The capacity of a pycnometer is selected according to the amount of the liquid and the desired measurement accuracy. If the liquid quantity is not limited, use should be made of the largest pycnome-

ter to obtain as accurate results as possible. In determining density with the aid of a pycnometer, the "water number" (mass of water within the pycnometer volume at 20°C) must be taken. To this end, pycnometers are thoroughly washed with a cleaning mixture, alcohol, and distilled water, dried and weighed on an analytical balance to within 0.0002 g. Then, they are filled with distilled water to a level slightly above the mark (the plug-type pycnometer is filled to capacity) and placed in a thermostat in which they are
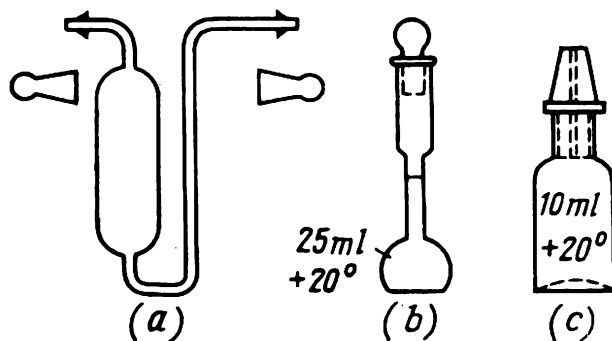
Fig. 108. Pycnometers for determining liquid density
a—U-tube; *b*—long-neck; *c*—plug-type

held at 20°C for 30 min. When the water level stabilizes, the water above the mark on the neck (with reference to the upper edge of the meniscus) is removed by means of a pipette or filter paper, and the inner surface of the neck is wiped clean. In plug-type pycnometers, the excess water flows out through the capillary and can also be removed with the aid of filter paper. The pycnometer with its plug or lid on and wiped dry on the outside is weighed to within 0.0002 g.

The water number M of a pycnometer is defined as the difference in mass between the pycnometer with water (G_2) and the empty one (G_1), in g, that is

$$M = G_2 - G_1. \qquad (5.15)$$

For density measurement, the test liquid is poured into a clean dry vessel (almost to capacity), the latter is tightly stoppered and held in a thermostat at 20°C. Then, the liquid is pipetted into a clean dry preweighed pycnometer with a known water number, which is followed by the same sequence of operations as during determination of the water number.

The liquid density is calculated using the formula

$$d_4^{20} = \frac{G_3 - G_1}{M} = (0.99823 - 0.0012) + 0.0012, \qquad (5.16)$$

where G_3 is the mass of the pycnometer with the liquid, in g; G_1 is the mass of the empty pycnometer, in g; M is the water number, in g; 0.99823 is the density of water at 20°C, and 0.0012 is the relative density of air at 20°C and 10^5 Pa.

Determination of Viscosity. Viscosity, or internal friction, is the capacity of a liquid to resist the mutual displacement of its particles (slip or shear) under the effect of applied forces. Viscosity is a highly important property of liquids, particularly in the case of petroleum products, primarily, lubricating oils. It is characterized by the viscosity coefficient and may be dynamic, kinematic or relative.

Dynamic viscosity is the viscosity of a flowing liquid in which the linear velocity has a gradient of 1 m/s over 1 m of the distance (grad u) normal to the shear plane, under the effect of a shear stress of 1 Pa. In the case of a laminar flow, dynamic viscosity is calculated using the Newton formula

$$\mu = F/S \ \mathrm{grad} \ u, \tag{5.17}$$

where $F/S = P_{sh}$ is the shear stress, in Pa.

The dynamic viscosity is commonly expressed in poises:

$$1 \ \mathrm{poise} = 1 \ \mathrm{dyne \cdot s/cm^2} = 1 \ \mathrm{g/(cm \cdot s)}.$$

The dynamic viscosity of water at 4°C is

$$1.005 \cdot 10^{-3} \ \mathrm{Pa/m^2} = 1.005 \ \mathrm{mPa/m^2} \approx 1 \ \mathrm{cP}.$$

Kinematic viscosity ν equals the ratio of the dynamic viscosity of a liquid or gas at a given temperature to its density at the same temperature:

$$\nu = \mu/\rho. \tag{5.18}$$

In the SI system, kinematic viscosity is expressed in terms of $\mathrm{m^2/s}$, that is the kinematic viscosity of a flow having a dynamic viscosity of 1 $\mathrm{Pa/m^2}$ and a density of 1 $\mathrm{kg/m^3}$.

In the CGS system, kinematic viscosity is expressed in stokes (St). A stoke represents the viscosity of a liquid whose density equals 1 $\mathrm{g/cm^3}$ and which offers a resistance of 1 dyne to the mutual displacement of two liquid layers having an area of 1 $\mathrm{cm^2}$, spaced 1 cm apart, and moving relative to each other at a velocity of 1 m/s:

$$1 \ \mathrm{St} = 100 \ \mathrm{cSt} = 1000 \ \mathrm{mSt}.$$

Relative viscosity RV is used primarily as a practical characteristic of petroleum products. The most common of the relative concepts is that of specific viscosity indicating the extent to which the dynamic viscosity of a given liquid is greater or smaller than that of a reference liquid (usually water) at an arbitrarily taken temperature, that is

$$\mathrm{RV} = \mu_t/\mu_{\mathrm{W}_{t_1}}, \tag{5.19}$$

where μ_t is the dynamic viscosity of a petroleum product at a temperature t, and $\mu_{\mathrm{W}_{t_1}}$ is the dynamic viscosity of water at a temperature t_1.

Relative viscosity is expressed in arbitrary units—degrees or seconds. These units represent the ratio of the time it takes for the test liquid to flow through an opening in the instrument used, at the test temperature t, to the time of flow of the reference liquid through the same opening at the same temperature. In some cases, relative viscosity is determined as the time it takes for a certain volume of the liquid to flow through the opening under standard conditions.
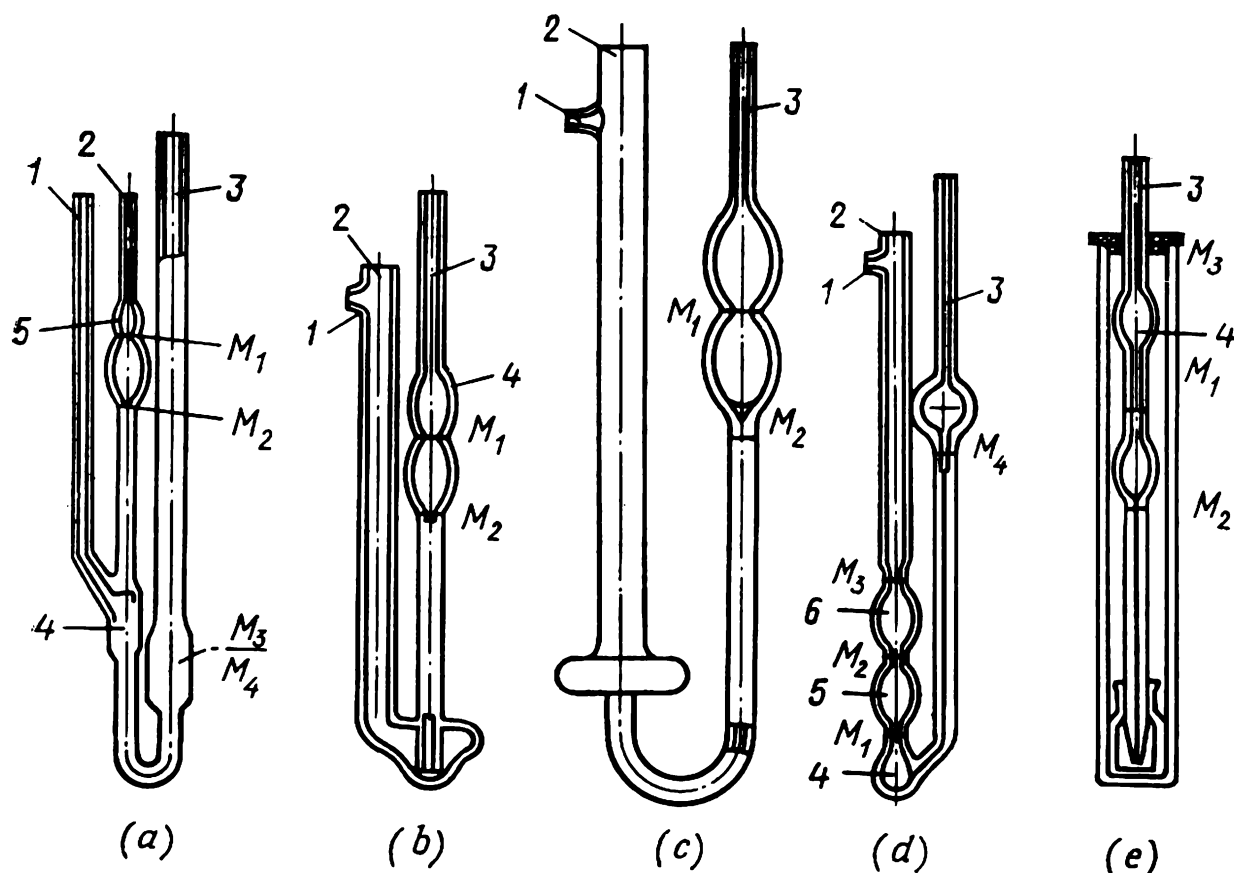
Fig. 109. Glass viscometer types
a—ВПЖ-1; b—ВПЖ-2; c—ВПЖ and Pinkevich; d—ВНЖ; e—ВПЖМ

The various types of viscometers are shown in Fig. 109. Viscometers of the ВПЖ-1 type are used to measure the viscosity of transparent (translucent) petroleum products; it is recommended to use these instruments at a positive temperature. ВПЖ-2 and Pinkevich viscometers are intended for measuring the viscosity of transparent (translucent) petroleum products at positive and negative temperatures. Viscometers of the ВНЖ type measure the viscosity of opaque (non-translucent) petroleum products. Viscometers of the ВПЖМ type are used to measure the viscosity of transparent (translucent) petroleum products taken in small amounts (1 cm³).

The viscometer for measuring the kinematic viscosity of a sample is selected such that the time it takes for the sample to flow through its opening is not less than 200 s. Before the measurement, the viscometer is thoroughly washed with a solvent and dried. Viscous

petroleum products are heated prior to testing to 50-100 °C, and the products containing moisture are desiccated with anhydrous Na_2SO_4 and filtered.

The viscometer with the test sample is placed in a thermostat. The vertical position of the capillary (ВПЖ-1, ВПЖ-2, ВПЖ-4, ВПЖМ, Pinkevich) or the wide tube (ВНЖ) is checked by a plumb line. In determining the viscosity at a temperature below the dew point, containers with calcium chloride are connected to the tubes
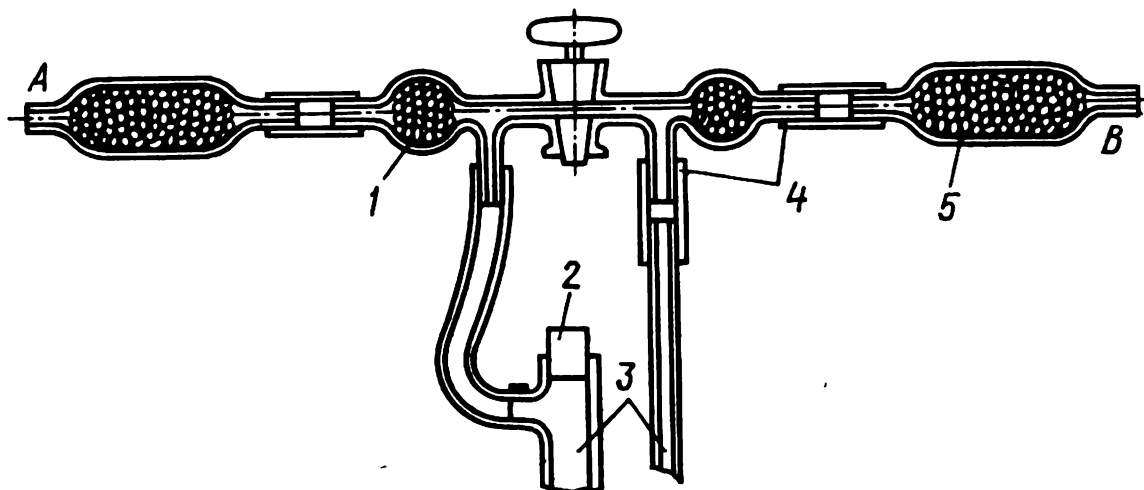
Fig. 110. Connection between desiccator and viscometer (ВПЖ-2, ВПЖ-4, Pinkevich)

1—cotton; *2*—plug; *3*—viscometer; *4*—rubber tubes; *5*—desiccator

to avoid water condensation in the instrument. Fig. 110 shows schematically the connection between a desiccator and the viscometer (ВПЖ-2, ВПЖ-4, Pinkevich).

To lift the liquid into the measuring cylinder, the cock is closed, and the rubber bulb connected to the tube A or B drives the liquid up. During measurement, the cock must be closed.

To measure the time of petroleum product flow in a ВПЖ-1 viscometer (see Fig. 109), the sample is poured into the clean viscometer through the tube *3* so that its level is between marks M_3 and M_4. Rubber hoses are fitted on the ends of the tubes *1* and *2*, the first hose having a pinchcock and a rubber bulb, while the other is provided only with a pinchcock. The viscometer is set upright in a liquid thermostat so that the level of the thermostat liquid is several centimetres above the bulb *5*. The viscometer is held at the test temperature for at least 15 minutes, then the liquid is sucked (by the rubber bulb), with the tube *1* closed, above the mark M_1 approximately up to the middle of the bulb *5*, and the cock associated with the tube *2* is closed. If the viscosity of the petroleum product is less than 500 cSt, the cock on the tube *2* is opened first, then that on the tube *1*. In the case of more viscous products, the tube *1* is opened first, then the time it takes for the liquid level in the tube *2*

to go down from the mark M_1 to M_2 is measured. In doing so, one must make sure that by the time the liquid level approaches the mark M_1, the liquid "hangs up" in the bulb *4* and the capillary contains no air bubbles.

To measure the time of flow of petroleum products in a viscometer of the ВПЖ-2, ВПЖ-4. or Pinkevich type, a rubber hose is fitted on the outlet port *1*. Then, the tube *2* is plugged by a finger, the viscometer is turned upside down, the tube *3* is immersed into a vessel with the petroleum product being tested, and the latter is sucked (with the aid of a rubber bulb, water-jet pump, or some other device) up to the mark M_2, making sure that no air bubbles form in the liquid. As soon as the liquid level reaches the mark M_2, the viscometer is withdrawn from the vessel and quickly turned back to the original position. The excess liquid is wiped off the outer side of the end of the tube *3*, and a rubber hose is fitted on it. The viscometer is put in a thermostat so that the bulb *4* is below the level in the thermostat. After the viscometer has been held in the thermostat for at least 15 minutes at a specified temperature, the liquid is sucked into the tube *3* approximately up to one third of the height of bulb *4*. The tube *3* is made to communicate with the atmosphere, and the time interval during which the meniscus of the liquid goes down from the mark M_1 to M_2 is determined.

To carry out the same measurement in a viscometer of the ВНЖ type, a rubber hose is fitted on the outlet port *1*. Tube *3* is plugged by a finger, the viscometer is turned upside down, immersed into a vessel with the petroleum product, and the latter is sucked by means of a rubber bulb, water-jet pump, or some other device up to the mark M_4 so that no air bubbles appear in the liquid. When the liquid level reaches the mark M_4, the viscometer is withdrawn from the vessel and immediately returned to the initial position. The excess liquid is removed from the outside of the end of tube *3*, and a rubber hose 8 to 15 cm long is fitted on it, the hose being provided with a pinchcock. The latter is opened to fill the bulb *6* with the liquid, and when the liquid level reaches approximately half the height of the bulb *6*, the cock is closed. The viscometer is placed in a thermostat, and after it has been held in the latter for a certain period of time (20 min), tube *3* is opened, and the time it takes for the liquid to rise from the mark M_1 to M_2 and from M_2 to M_3 is recovered using two stopwatches.

The viscosity of the liquid is calculated from the time of filling of the bulb *5*. The measured time of filling of the bulb *4* serves as a reference. The values of viscosity, calculated from the times of filling of bulbs *5* and *4*, may differ by up to 2% and even up to 3% when the measurement is made at a temperature below 15°C.

To measure the time of flow of petroleum products through a viscometer of the ВПЖМ type, it is filled as follows: the pipette *3*

is immersed into the liquid to a depth of 1 to 2 mm, and the liquid is sucked up to the mark M_3. The tip of the pipette is wiped to remove the suspended liquid drop, and the pipette is carefully lowered into the receiver. The instrument is assembled as shown in Fig. 109e and placed in a thermostat. The measurement is made after it has been held in the thermostat for at least 30 minutes. To do this, the liquid is raised up to bulb *4* or even higher by means of the rubber hose and bulb connected to the upper end of the pipette, then the pipette is made to communicate with the atmosphere. The time it takes for the liquid to flow from the mark M_1 to M_2 is measured.

In all viscometers, except for ВНЖ the liquid flow time is measured 3 to 5 times, then the arithmetic mean of the time of sample flow through the viscometer is calculated. The kinematic viscosity of the sample is calculated using the formula

$$\nu = c\tau \ (g/980.7) \ K, \qquad\qquad (5.20)$$

where *c* is the viscometer constant, in cSt/s (specified in the test certificate), τ is the arithmetic mean of the time of sample flow through the viscometer, in s; *g* is the free fall acceleration at the point of viscosity measurement, in cm/s^2; 980.7 is normal acceleration, in cm/s^2; and *K* is a coefficient taking into account the variations in the hydrostatic pressure of the liquid as a result of its expansion when heated by Δt, $K = 1$ for viscometers of the ВПЖ-1 type, $K = 1 + 0.000040$ for viscometers of the ВПЖ-2, ВПЖ-4 and Pinkevich types; $K = 1 + 0.000087$ for viscometers of the ВНЖ type; and $K = 1 + 0.000074$ for viscometers of the ВПЖМ type; Δt is the difference between the sample temperature when the viscometer is being filled and that during viscosity measurement.

The conversion of kinematic to relative viscosity is represented in Table 18. At higher kinematic viscosities, use can be made of the formula

$$RV = 0.135\nu. \qquad\qquad (5.21)$$

Table 18

cSt	RV degrees	cSt	RV degrees	cSt	RV degrees
1.0	1.00	8.0	1.67	60.0	8.13
2.0	1.10	9.0	1.76	70.0	9.48
3.0	1.20	10.0	1.86	80.0	10.80
4.0	1.29	20.0	2.95	90.0	12.20
5.0	1.39	30.0	4.20	100.0	13.50
6.0	1.48	40.0	5.50	110.0	14.90
7.0	1.57	50.0	6.81	120.0	16.20

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Instructions to the Laboratory Work "Determination of Dispersity, Density of Solid Loose Materials, Density and Viscosity of Liquids"

1. Make sure that the experimental setup and instruments are ready for operation.

2. Carry out all experiments involving organic liquids in electric heaters with enclosed coils.

3. **Handle mercury under an exhaust hood.**

4. Keep mercury instruments and vessels on a tray with high edges. Carefully collect spilled mercury with a metal brush.

5. Carry out all analyses using standard pycnometers, hydrometers and other instruments.

6. In determining the density of highly viscous products, heat them to 50-60°C before filling the pycnometer.

7. Do not use hydrometers (oil hydrometer) for determining the density of highly volatile liquid petroleum products (e.g., petroleum ether, etc.).

8. In determining the density of petroleum products having a viscosity higher than 200 cP, dilute them with an exactly equal amount of kerosene whose density must be measured by the same hydrometer.

LABORATORY WORK 32. ANALYSIS OF THE POROUS STRUCTURE OF SOLIDS

The most important characteristics of solid materials—reagents, catalysts, and adsorbents—include their porous structure (surface, total volume of pores, and their size distribution).

The specific surface of solid dispersed materials is the total surface of solid particles per unit mass or volume of the material. The surface of non-porous and porous solids differs widely in extent; in the case of porous materials, it can exceed that of non-porous ones by one to three orders of magnitude.

The surface of non-porous materials, usually amounting to less than 1 m²/g, depends on the granulometric composition and can be roughly estimated from sieve analysis data; a more accurate estimation is provided by sedimentation analysis based on the different rates of descent of grains in a liquid, depending on their size, or by separation analysis in which the separation into fractions is achieved by means of an air jet of a particular velocity. Both methods of determining the surface are based on the fundamental postulates of the Stokes law.

For many porous materials, including the widely used solid catalysts and sorbents, the specific surface is a highly significant characteristic, and its exact determination is a matter of para-

mount importance. The specific surface of porous solids is determined, primarily, by the size and number of pores. The comminution of a material is insignificant because the outer surface is negligibly small as compared to the pore surface. There are several methods of rough estimation of the overall or total porosity of a solid.

The *volumetric method* is based on determination of the volume of water, necessary to fill the pores. A dry porous powder, to which small amounts of water are added, retains its looseness to some extent, when shaken, till the liquid fills all the pores. Further addition of water leads to coalescence and caking of the particles. The total pore volume v_p (cm^3/g) is defined as the ratio of the water volume W involved in wetting the material to the sample weight:

$$v_p = W/g. \tag{5.22}$$

The *gravimetric method* resides in boiling a dried sample with water for two hours. The weight G (in g) of the absorbed water is determined from the formula

$$G = (g_1 - g_0)/g_0, \tag{5.23}$$

where g_1 and g_0 stand for the weights of the test sample before and after saturation, respectively, in g.

The total pore volume v_p can be determined more accurately from the true (d) and apparent (ρ_{app}) densities:

$$v_p = \frac{1}{\rho_{app}} - \frac{1}{d}. \tag{5.24}$$

The size distribution of pores in solid porous materials is important from the standpoint of pore diffraction kinetics of processes. The function of size distribution of pores can be determined by the adsorption method based on the hysteresis involved in the capillary condensation of gases in the adsorbent pores. To ensure the desired accuracy in deriving the adsorption isotherms, the adsorption is measured gravimetrically using a spring McBain balance. This technique is recommended for measuring pores with diameters ranging from 15 to 200 Å. To measure pores with diameters ranging from 30 to 30 000 Å, the capillary-condensation method can be replaced by forcing mercury into the pores of a solid.

The most reliable ways to determine the specific surface of solid materials are the adsorption methods enabling measurement of the volume (weight) of the adsorbed gas forming a monomolecular layer on the surface of interest. Nitrogen is often used as the adsorbate. The adsorption methods are divided into three main groups: volumetric, gravimetric, and conductometric.

The classic *volumetric method* is the one proposed by Brunauer, Emmett, and Teller (B.E.T. method). According to the B.E.T. equation, the volume of the gas adsorbed by the surface of solid

particles (in the form of a monomolecular layer) varies with the adsorbent surface:

$$v = \frac{p}{p_{\text{sat}}\left(1 + \dfrac{p}{p_{\text{sat}}}\right)} = \frac{1}{v_{\text{mol}}c} + \frac{c+1}{v_{\text{mol}}c\,p_{\text{sat}}}\,p, \qquad (5.25)$$

where v is the volume of adsorbed vapours under normal conditions; v_{mol} is the volume of adsorbed vapours, necessary for formation of the monomolecular layer; p is the pressure of the vapours that are at equilibrium with the adsorbed layer; p_{sat} is the saturated vapour pressure at the isotherm derivation temperature; and c is a constant.

The *gravimetric method* is based on an increase in the weight of the adsorbent-adsorbate solid phase as a result of gas adsorption.

In *conductometric methods* use is made of a cell enabling the heat conductivity of the gas flowing over the sorbent to be determined with the gas composition varying as a result of adsorption or desorption.

In recent years, the chromatographic method has been gaining in acceptance. It does not require vacuum devices and is advantageous over other methods by a simpler setup and a comparatively more rapid determination.

A. ANALYSIS OF POROUS STRUCTURE USING AN ADSORPTION VACUUM SYSTEM WITH A QUARTZ SPRING BALANCE

Experimental Setup and Procedure

The experiment with the vacuum system includes several steps: (a) evacuation; (b) measurement of the adsorption isotherm; and (c) derivation of the desorption branch of the isotherm.

Evacuation. The vacuum system is shown schematically in Fig. 111. A 0.1-g sample weighed on an analytical balance is placed in a cup *3*. The sensitivity of the quartz spring *2* varies from *2* to *5* mg/mm. The roughing-down pump is switched on after closing all the cocks providing communication with the atmosphere. The cock *B* is opened, and the fore-vacuum vessel *4* for the McLeod gauge *5* is evacuated. The cock *D* is fully opened. The mercury level is alternately raised (by slightly opening the cock *E*) up to *b-b* and lowered (by means of the cock *C* associated with the fore-vacuum vessel *4*) down to *a-a* until it stabilizes at *a-a* in the McLeod gauge. Next, the system continues to be evacuated with the cock *E* in the fully open position (for 5 min), all cocks and ground joints being thoroughly sealed. The cocks *D* and *E* are then closed, the roughing-down pump is switched off, the cock *A* is quickly opened to let air in, and the position of the cups *3* in the sorption tubes *1* is measured by a cathetometer. Electric heaters are fitted on the sorption tubes, the desired

temperature is preset at the automatic potentiometer, and the rough-ing-down pump continues the evacuation. The residual pressure in the system is measured by the McLeod gauge. To this end, the cock C is turned to align its port with the air line, and the mercury in the open capillary of the gauge is raised up to the level of the sealed capillary, the difference between the mercury levels in both capillaries is measured by the cathetometer, and the mercury level is
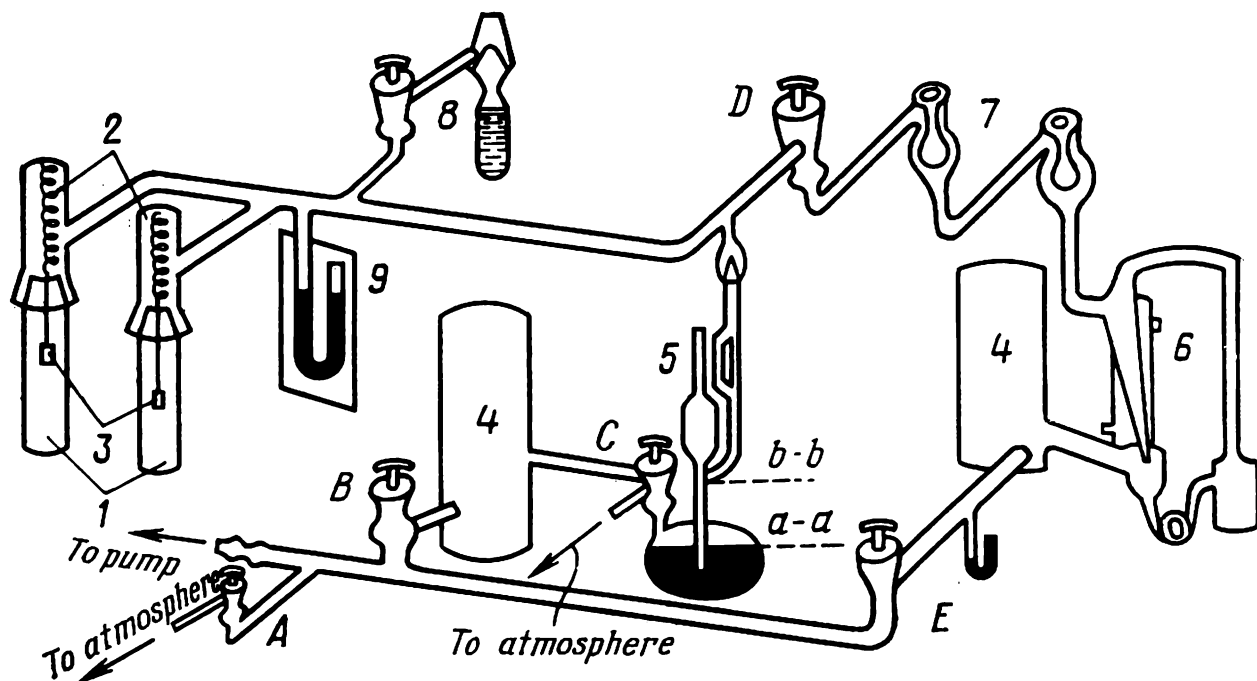
Fig. 111. Adsorption vacuum system with quartz spring balance

brought down to *a-a*. The residual pressure *P* is calculated from the equation

$$P = h^2 + S/ (V + v), \tag{5.26}$$

in which *h* is the difference between the mercury levels in the open and sealed capillaries, in m; *S* is the capillary cross-section, in m^2; *V* is the gauge bulb volume, in m^3; and *v* is the volume of the sealed capillary, in m^3.

After the pressure has reached approximately 0.13 Pa (10^{-3} mm Hg), the mercury diffusion pump *6* is activated, water is fed into the cooling jacket of the pump, liquid nitrogen is poured into the traps *7*, and the heating coil is energized. Once the pressure has reached $0.13 \cdot 10^{-3}$ Pa (after 6 to 8 h), the electric heaters are removed, and the position of the cups *3* is measured by the cathetometer.

Measurement of the Adsorption Isotherm. The measurement boils down to determination of the sample weight increment as a function of the overlying adsorbate vapour pressure. The cock *D* is closed, a metered amount of the adsorbate is supplied from the dispenser *8* (Table 19), and the adsorbate vapour pressure is measured. The

heating of the diffusion pump is switched off, and, after the pump has cooled, the water supply into the cooling jacket is cut off. The measurement of the first point of the adsorption isotherm is followed by that of the second and subsequent points. Each time the adsorption equilibrium is established (the springs stop being stretched), the new position of the cups is measured along with the new equilibrium vapour pressure. The temperature of the adsorbate vapours and samples is maintained constant (about 20°C) throughout the experiment. The pressure is first measured by the McLeod gauge, then by the U-tube manometer *9*.

Table 19

Adsorbate	Molecular weight	$d \cdot 10^{-3}$, kg/m³	$P_{sat}^{20} \cdot 10^{-4}$, Pa	$\theta_{mol} \cdot 10^{20}$, m²	$N_A \theta_{mol} \cdot 10^{-6}$, m²/mole	$\sigma \cdot 10^3$, N/m	$v_0 \cdot 10^3$, m³/mole	$\dfrac{\sigma v_0 10^{10}}{RT}$, m
Methanol	32.04	0.792	1.27	25	1.51	22.60	40.42	3.74
Benzene	78.11	0.879	1.00	49	2.96	28.88	88.86	10.5
Carbon tetrachloride	153.8	1.595	1.23	37	2.23	25.80	96.54	10.2
n-He-xane	86.2	0.660	1.62	51.5	3.11	18.43	130.76	9.9
Water	18.01	1.00	0.23	25	1.51	72.80	18.06	5.4

The last point of the adsorption isotherm is determined at an equilibrium pressure close but not equal to the pressure of saturated adsorbate vapours at 20°C. This is done to avoid condensation of adsorbate vapours on the walls and cups even at a slight drop in the experimental temperature, hence to avoid errors in determining the equilibrium amount of adsorption at $P/P_{sat} \approx 1$.

Plotting the Desorption Branch of the Isotherm. The roughing-down pump is switched on, the cock *E* is opened, and the fore-vacuum vessel *4* is evacuated. Then, the pump is switched off, the cock *D* is partially opened, and the mercury level in the gauge *5* is lowered to the required pressure. Lowering the adsorbate vapour pressure leads to partial desorption of the previously adsorbed substance, hence, to compression of the spring. Once the equilibrium has been established, the cup position and pressure are measured. With the vapour pressure being gradually decreased, the desorption branch of the isotherm from $P/P_{sat} \simeq 1$ to the P/P_{sat} corresponding to the point of closure of the hysteresis loop is determined (Fig. 112).

To bring the system under atmospheric pressure, the cocks *D* and *A* (see Fig. 111) are opened. It is established by gradually raising

(by letting in air through the cock C) the mercury level in the McLeod gauge up to b-b and lowering it (by the cock E) down to a-a. All cocks except for B are opened, the ground joints of the sorption tubes are carefully turned to remove the tubes, and fresh samples are put into the cups.
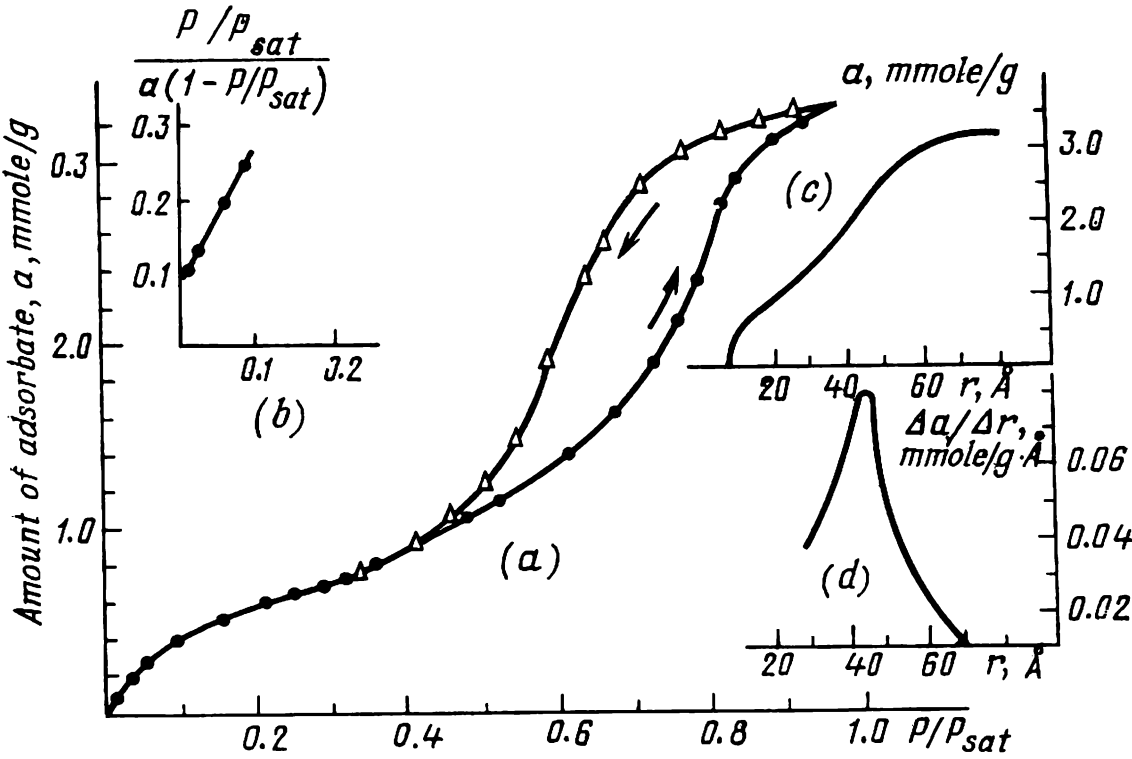
Fig. 112. Isotherm of benzene vapour adsorption on active alumina (a) and its rectification in the coordinates of the B.E.T. equation (b); structural curve (c) derived from the desorption branch of isotherm (a) and differential curve of distribution of the adsorbate amount over predominant pore radii (d), derived from curve (c)

The P/P_{sat} and a measurement results are tabulated as follows:

Adsorption				Desorption			
Point number	P, Pa	P/P_{sat}	a, mmole/g	Point number	P, Pa	P/P_{sat}	a, mmole/g

and curves are plotted.

The plot of the experimental data has the amount of the adsorbed substance (a) on the x-axis and the relative vapour pressure (P/P_{sat}) on the y-axis.

Determination of Specific Surface. The determination of S_{sp} (m²/g) from adsorption data boils down to that of the monomolecular layer capacity a_{mol}, that is the amount of the adsorbed substance cover-

ing the surface in a dense monomolecular layer:

$$S_{sp} = a_{mol} N_A \theta_{mol}, \qquad (5.27)$$

where N_A is the Avogadro constant, and θ_{mol} is the area occupied by an adsorbate molecule in the monomolecular layer on the adsorbent surface, in m^2.

The value of a_{mol} can be determined from the linear form of the B.E.T. isotherm equation (5.25):

$$\frac{P/P_{sat}}{a(1-P/P_{sat})} = \frac{1}{a_{mol}C} + \frac{C-1}{a_{mol}C} \cdot \frac{P}{P_{sat}}, \qquad (5.28)$$

where a is the amount of the substance adsorbed at the relative pressure P/P_{sat}, in mmole/g, and C is a constant related to the heat of adsorption and temperature.

The adsorption isotherm is represented in the coordinates

$$\frac{P/P_{sat}}{a(1-P/P_{sat})} - P/P_{sat}$$

(Fig. 112), and use of the B.E.T. equation gives a straight line with a slope $(C-1)/a_{mol}C$, intercepting $1/a_{mol}C$ on the x-axis. Thus, a_{mol} is found. The rectilinear portion usually corresponds to the P/P_{sat} range of 0.01 to 0.3-0.35.

Example. Figures 112 represents the isotherm of adsorption of benzene vapours on active alumina. S_{sp} can be calculated from this isotherm. At $(C-1)/a_{mol}C = 0.110$ and $1/a_{mol}C = 0.08$, we have $a_{mol} = 0.526$ mmole/g. Substitution of these values into Eq. (5.27) gives $S_{sp} = 155$ m^2/g.

The basic constants of the most commonly used adsorbates, necessary for calculation of the porous structure parameters from adsorption isotherms, are listed in Table 19.

Calculation of the Equivalent Pore Radius and Total Pore Volume. The equivalent pore radius is calculated from the desorption branch of the isotherm, using the Thomson-Kelvin equation

$$r_p = \frac{2\sigma v_0}{2.3 RT \log(P_{sat}/P)}, \qquad (5.29)$$

where σ is the surface tension of the liquid whose vapours are adsorbed, in N/m, and v_0 is the molar volume of the liquid, in m^3/kmole.

In calculating the pore radius, the amount a of the adsorbed substance in the liquid state is plotted as a function of the calculated pore radius r (Fig. 112c). Derived from the resulting curve is the differential $\Delta a/\Delta r - r$ curve (Fig. 112d). The obtained value of r_{max} must be increased by the statistical thickness δ of the adsorbed layer at a vapour pressure corresponding to the onset of capillary condensation. In the case of homogeneously porous samples, the value of δ can be determined with a satisfactory degree of accuracy by dividing the amount a of the substance, adsorbed by the beginning of the

hysteresis, by the specific surface

$$\delta = av_0/S_{sp}. \qquad (5.30)$$

For example, if $a = 0.85$ mmole/g, $v_0 = 88.86$ m^3/kmole, and $S_{sp} = 155$ m^2/g, then $\delta = 5$ Å. Consequently,

$$r = r_{max} + \delta = 46 + 5 = 51 \text{ Å}.$$

The total pore volume (v_p) of a dispersed sample is determined from the equation $v_p = a_{sat}v_0$, a_{sat} being the amount of the substance adsorbed at $P/P_{sat} = 1$.
Hence,

$$v_p = 3.27 \cdot 10^{-3} \cdot 88.86 = 0.291 \text{ cm}^3/\text{g}.$$

LITERATURE

Yermolenko, N. F. and Efros, M.D., *Controlling the Porous Structure of Oxide Adsorbents and Catalysts*, Minsk, 1971.

Experimental Techniques in Adsorption and Molecular Chromatography/Ed. by Kiselev, A. V. and Dreving, V. P., Moscow, 1973.

Instructions to the Laboratory Work "Analysis of Porous Structure Using an Adsorption Vacuum System with a Quartz Spring Balance"

1. Before the experiment, check the earthing of the roughing-down pump and heaters, as well as the insulation of electric cables.
2. Do not heat the cocks with an open flame before and after the grease is applied.
3. Open the cocks slowly and smoothly, by turning them without pressure and by supporting the cock sleeve with the other hand.
4. Do not open the cock on the line between the fore-vacuum vessel and the McLeod gauge simultaneously with the cock on the line between the other fore-vacuum vessel and the diffusion pump. When one of the fore-vacuum vessels is being evacuated, the cock on the line to the other fore-vacuum vessel must be closed.
5. When measuring by the McLeod gauge, raise the mercury level very slowly, otherwise the pulsating motion of the mercury with the latter impinging upon the vessel and tube walls may lead to an accident.
6. Strictly follow the sequence of switching the diffusion pump on and off:
(a) swith on the diffusion pump 30 minutes after the roughing-down pump has been started, the **water cooling being activated first** and then the heating,
(b) switch off the diffusion pump in the reverse order: first **stop the heating**, then, after the mercury vessel has cooled completely, **stop the water cooling** and only after that **switch off the roughing-down pump.**
7. Before switching on the roughing-down pump, close the cock on the line through which the pump communicates with the atmosphere. Before the pump is switched off, open the cock to avoid suction of the oil into the system.
8. Do not leave the working pumps unattended in view of their possible outage as a result of power failure or interrupted flow of tap water into the cooling jacket of the diffusion pump.
9. In the case of power failure or the drive belt on the roughing-down pump coming off: (a) shut all the cocks in the system; (b) throw out the rotary switch on the wall-mounted electric board; and (c) open the cock on the line through which the roughing-down pump communicates with the atmosphere.

10. In the case of emergency cutoff of the water supply: (a) shut the cock on the line between the diffusion pump and the evacuated part of the system; and (b) de-energize the heater of the diffusion pump.

Do not switch off the roughing-down pump!

11. For personnel protection in the event of an accident, the system under high vacuum is enclosed in acrylic plastic boxes. Run the system under high vacuum only with the front wall of the box closed.

12. To avoid spillage of mercury on the floor in an accident, the system must be mounted on metal oil-painted trays with high edges.

Handle mercury (when filling the instruments, etc.) in compliance with the "Rules for Safe Handling of Mercury" (see "Safety Rules to Be Observed in a Chemical Laboratory").

13. Do not use benzene for cleansing and degreasing the system components, for removing lubricating oils from cocks, and for washing hands.

14. Handle liquid nitrogen (taking it from the Dewar flask, filling the trap) wearing a protective acrylic plastic mask and cloth gloves.

15. Handle all glass components of the system (fitting vacuum hoses on the tubes and removing them, lapping the cocks, etc.) with your hands protected against cuts (gloves, towel).

B. ANALYSIS OF SECONDARY STRUCTURE OF POROUS SOLIDS BY MERCURY POROMETRY

Mercury porometry is based on the property of mercury not to wet many solids. The relationship between ambient pressure and the capillary resistance in the pores of a solid is expressed by the following equation of capillary depression:

$$Shg\rho = -\Pi\sigma \cos \theta_w \qquad (5.31)$$

where S is the cross-sectional area of a pore, in m^2; h is the height of capillary depression of a liquid, in m; g is the free fall acceleration, in kg/m^3; ρ is the liquid density, in kg/m^3; Π, is the pore perimeter in m; σ is the surface tension of the liquid, in N/m; and θ_w is the wetting angle ($145°$ for silica gel, $142°$ for charcoal).

Since $hg\,\rho = P$, then $SP = -\Pi\sigma \cos \theta_w$, or

$$\frac{S}{\Pi} = -\frac{\sigma \cos \theta_w}{P}.$$

The ratio of the pore cross-sectional area to pore perimeter is what is known as hydraulic radius r_h which is always equal to half the equivalent pore radius r at any cross-sectional shape:

$$r_h = \frac{r}{2} = -\frac{\sigma \cos \theta_w}{P}, \qquad (5.32)$$

$$r = -\frac{2\sigma \cos \theta_w}{P}. \qquad (5.33)$$

The porous structure of solids is examined using a mercury porometric device comprising low- and high-pressure porosimeters. They enable measurement of equivalent pore radii ranging from 30 to 350 000 Å.

Experimental Setup and Procedure

The *low-pressure porosimeter* is intended for evacuation of samples, filling them with mercury, and determining the volume of the larger pores. A porosimeter (Fig. 113) consists of a glass cylinder *22* with sealed-in nichrome wires, a dilatometer *21*, a mercury container *8*, a McLeod gauge *12*, a mercury gauge *2*, a diffusion pump *19*, a roughing-down pump, and a resistance bridge.
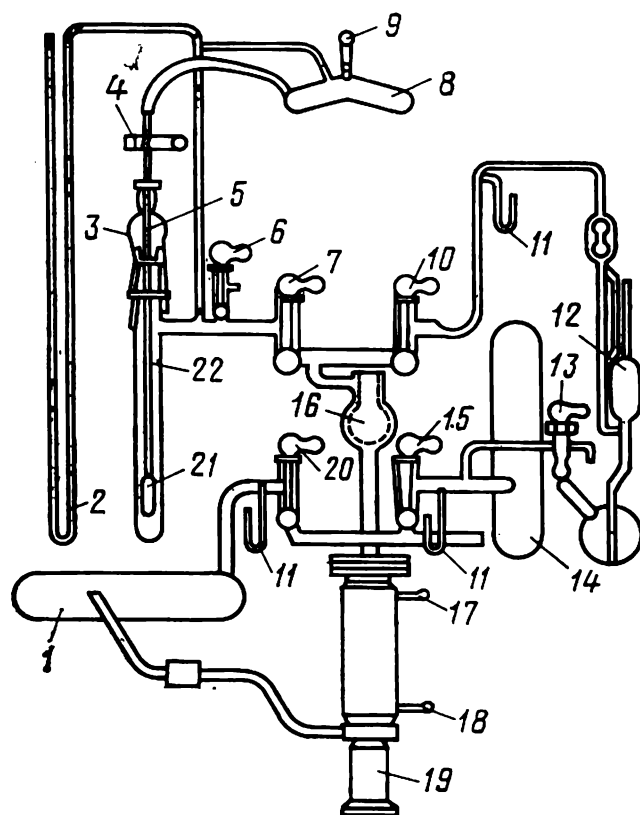
Before the experiment, the test sample is dried to a constant mass and placed in the dilatometer which is essentially a glass capsule gradually changing to a capillary. The capillary terminates in an acrylic plastic head with two nichrome contacts. A glass partition is sealed in between the capsule and capillary, passing through which is a platinum-iridium wire whose ends are screw-clamped to the dilatometer contacts. The dilatometer is weighed on a counter balance and placed in the cylinder *22* of the porosimeter. The dilatometer contacts are connected to the cylinder contacts *3*, and the electric circuit is tested by the resistance bridge. Then, all cocks are closed, the three-way cock is opened for the roughing-down pump to communicate with the instrument, and the pump is switched on. The cocks *7*, *15*,

Fig. 113. Low-pressure porosimeter

1—fore-vacuum vessel; *2*—pressure gauge; *3*—cylinder ¡contacts; *4, 6, 7, 10, 13, 15, 20*—cocks; *5*—capillary for feeding mercury; *8*—mercury container; *9*—plug; *11*—mercury gauge; *12*—McLeod gauge; *14*—fore-vacuum vessel; *16*—mercury vapour trap; *17*—water discharge tube; *18*—water feed tube; *19*—diffusion pump; *21*—dilatometer; *22*—porosimeter cylinder

20, and *10* are slowly opened. After 25 to 30 minutes, the roughing-down pump still running, the diffusion pump *19* is switched on after its cooling jacket has been filled with water. For complete evacuation of thermally stable solids, the cylinder of the porosimeter is heated in an electric tube furnace to 250-300 °C. For complete deaeration of the mercury in the container *8*, it is transferred from one end of the container to the other several times. After the diffusion pump has run for half an hour, the residual air pressure in the porosimeter is measured by the McLeod gauge. As soon as the pressure reaches $1 \cdot 10^{-4}$ mm Hg ($10^{-4} \cdot 133.3$ Pa), the heating of the sample is discontinued, the furnace is lowered, and after 40 to 50 minutes the dila-

tometer starts being filled with mercury. To do this, the container *8* is tilted, the cock *4* is closed, and the container *8* is brought back to the initial position. Next, the cocks *7* and *10* are closed, the diffusion pump *19* is switched off, the cock 20 is closed, the three-way cock is turned for the roughing-down pump to communicate with the atmosphere, and the pump is switched off.

After the roughing-down pump has been switched off, the mercury column in the dilatometer is measured from the capillary tip to the
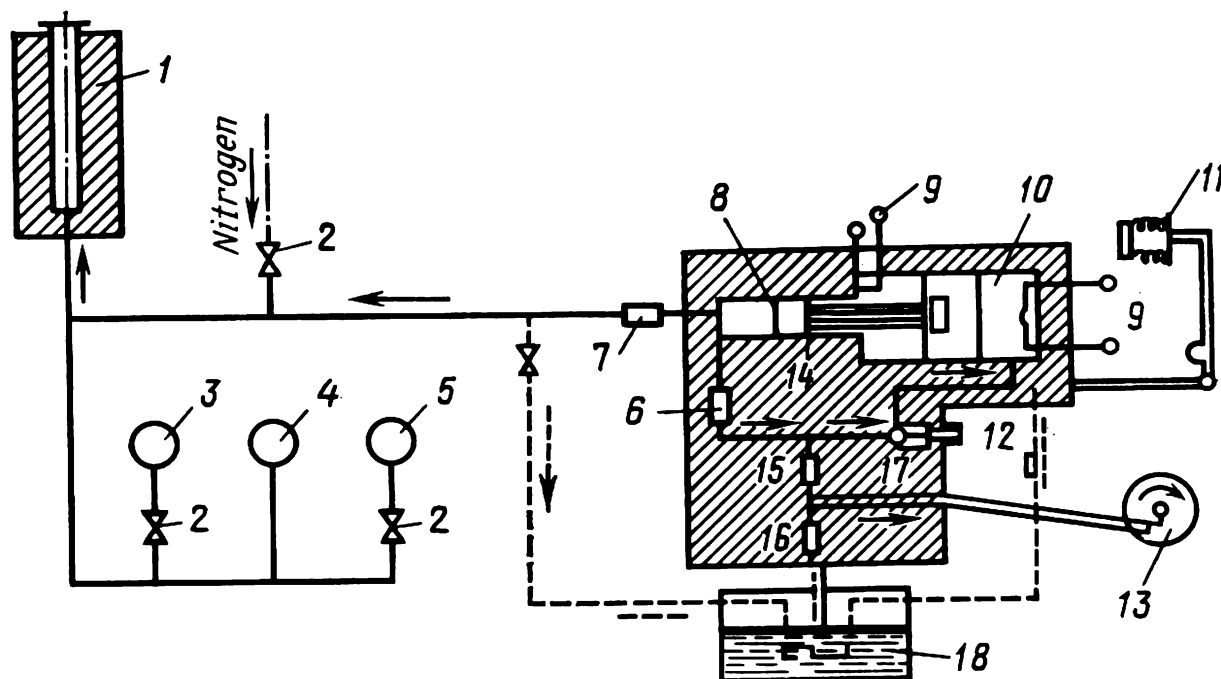
Fig. 114. High-pressure porosimeter

1—bomb; *2*—cock; *3, 4, 5*—pressure gauges rated at 25, 3000, and 250 kgf/cm², respectively; *6, 7*—check valves; *8*—high-pressure cylinder; *9*—electric contact; *10*—low-pressure cylinder; *11*—electromagnet; *12*—safety valve; *13*—electric motor; *14*—pump; *15*—delivery valve; *16*—suction valve; *17*—reducing valve; *18*—oil tank; ———— pressurized oil line; — — — non-pressurized oil line

head, along with the resistance in the electric circuit of the porosimeter. After 2 to 3 minutes, the resistance is measured again and, if the reading is the same, recorded. Then, air is let into the porosimeter, and the cock 6 is turned to bring the pressure in the porosimeter up to 100 mm Hg. At the same time, part of the mercury fills the larger pores of the sample, and the resistance R_1 of the platinum-iridium wire changes. The pressure in the porosimeter is raised to the atmospheric level, and each 100 mm Hg increment is followed by measurement of the equilibrium resistance in the electric circuit. After the atmospheric pressure has been attained, the dilatometer is transferred from the low-pressure porosimeter to the high-pressure one.

The *high-pressure porosimeter* is intended to measure the volume of pores ranging from 60 000 to 30 Å in size. It consists (Fig. 114) of a steel bomb *1* with a jacket, an oil pump, a pressure amplifier, three pressure gauges *3, 4,* and *5*, a resistance bridge, and a dilatome-

ter (the latter two are not shown). The pressure of 60 to 70 kg/cm²* is built up in the bomb by nitrogen fed from a bottle. The further boost in pressure is achieved by the oil pump. The piston of the oil pump is driven by an electric motor *13*.

The dilatometer is screwed to the contacts on the bomb plug, and the dilatometer with the plug on top is placed inside the bomb. The contacts on the bomb plug are connected to the d-c bridge, and the electric circuit is tested. Next, the bomb is closed by a locking nut. Before the pressure is raised, the initial resistance of the electric circuit is measured, the "nitrogen" and "oil drain" cocks are closed, and the cock *2* is opened.

The "nitrogen" cock is slowly opened to raise the pressure in the bomb to the prescribed level. As soon as this pressure is reached, the "nitrogen" cock is closed, and the resistance of the electric circuit is measured. After the first measurement the pressure is raised again, and each time the resistance is measured. When the pressure becomes 15-20 kg/cm², cock *2* is closed, and the rising pressure is monitored by the 250-kg/cm² gauge. As soon as the pressure reaches the 250-kg/cm² mark, cock *2* is closed again, and the subsequent rise in pressure is monitored by the 3000-kg/cm² gauge. When no more nitrogen is taken from the bottle, the "nitrogen" cock is shut, and the oil pump is started by hitting the "start" button to the right of the porosimeter. The moment the specified pressure is attained, the "stop" button is depressed, the oil supply into the bomb is cut off, and the resistance of the electric circuit is measured at the achieved equilibrium. The pressure in the bomb is reduced by slightly turning the "oil drain" cock counterclockwise, and the pressure drop is monitored by the high-pressure gauge.

When the bomb pressure becomes normal, the cap is removed, the electric circuit is disconnected from the bomb plug, the locking nut of the bomb head is turned off by 10 to 15 mm, then the main nut is screwed on the threaded portion of the plug till the nut rotates freely. After that, the main and locking nuts are turned off, the plug with the dilatometer are withdrawn from the bomb, the dilatometer is cleaned from oil, the capsule of the dilatometer is opened, and the mercury together with the sample are removed from the capsule.

The volume and radius of pores in the test sample are calculated from the volume v_{Hg} of the mercury filling the sorbent pores at a given bomb pressure (cm³), using the formula

$$v_{Hg} = K_d (R_c - R_0), \tag{5.34}$$

where K_d is the dilatometer constant (cm³/ohm) determined by special calibration of the dilatometer—it is indicative of the pore-

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* The high-pressure porosimeter is provided with pressure gauges calibrated to read in kg/cm², therefore, for conversion to the SI system, the pressure reading must be multiplied by $9.81 \cdot 10^4$, and the result will be pressure in pascals.

filling mercury volume at which the electric circuit resistance changes by 1 ohm; R_c is the resistance of the electric circuit, in ohms; and R_0 is the initial circuit resistance, in ohms. The pore volume per gramme of the test sample is determined from the formula

$$v_p = (v_{Hg} - \Delta v)/g, \qquad (5.35)$$

where Δv is the correction for compression of the overall mercury volume in the dilatometer, introduced (beginning from the pressure of 10 kg/cm²) for a given pressure, in cm³/g:

$$\Delta v = G_{Hg} N_p, \qquad (5.36)$$

where G_{Hg} is the mass of the mercury in the dilatometer, in g, and N_p is the mean correction factor at a respective pressure.

The equivalent radius r_p (Å) of the pores filled at a given pressure p is given by

$$r_p = \frac{2\sigma \cos \theta_w}{980.665 \cdot 10^3 P_{red}} = \frac{10^8 \cdot 2 \cdot 470.9 \cos 145}{10^3 \cdot 980.665 P_{red}} = \frac{75\,677}{P_{red}}, \qquad (5.37)$$

where P_{red} is the reduced pressure, in kg/cm², σ is the surface tension of mercury at 25°C, equal to 470.9 dyne/cm; and θ_w is the wetting angle;

$$P_{red} = P_{+i} - h'. \qquad (5.38)$$

The pressure including the initial one is

$$P_{+i} = P_{meas} + P_i, \qquad (5.39)$$

P_{meas} being the measured (gauge) pressure, in kg/cm²;

$$P_i = \frac{(P_{bar} + H)\,1.0333}{760} = 0.00135\,(P_{bar} + H), \qquad (5.40)$$

where P_{bar} is the barometric pressure, in mm Hg (1 mm Hg = 133.3 Pa); $H = h_1 + h_2$, h_1 being the height of the mercury column in the capillary of the dilatometer at the beginning of the experiment, in mm, and h_2 being the difference in the mercury levels in the U-tube manometer of the low-pressure porosimeter, in mm.

For the low-pressure porosimeter

$$P_{+i} = \frac{H\,1.0333}{760} = 0.00135\,H; \qquad (5.41)$$

$$h' = \frac{(R_c - R_0)\,10}{l}\,\frac{1.0333}{760}\ \text{kg/cm}^2; \qquad (5.42)$$

h' being the pressure decrement of the mercury column in the capillary of the dilatometer, in kg/cm². h' is calculated up to $P \sim \ \sim 10$ kg/cm²; l is the resistance of 1 cm of the Pt-Ir wire of the dilatometer, in ohms. For Pt-Ir wire, $l = 0.9852$.

When the integrated program is represented graphically, the pre volume v_p is plotted on the ordinate, and the logarithms of the equivalent pore radii are plotted on the abscissa.

The results are tabulated as follows:

Sample . . . .
Sample weight . . . .
Height of the mercury column in the capillary of the dilatometer
Weight of the dilatometer with the sample . . . .
Weight of the dilatometer with the sample and mercury . . . .
Atmospheric pressure in the experiment with the low-pressure porosimeter . . . .

h_1, mm	P_1, kg/cm²	R, ohm	$R_c - R_0$	P_{+i}, kg/cm²	h'	R_{red}, kg/cm²	r, Å	$\log r$	v_{Hg}, cm³	Δv	$v - \Delta v$, cm³	v_p, cm³/g

For conversion of the pore volumes expressed in different units (cm³/g, cm³/cm³), one must use the expression for apparent density

$$v_p \ (\text{cm}^3/\text{cm}^3) = v_p \ (\text{cm}^3/\text{g}) \cdot \rho_{\text{app}} \ (\text{g/cm}^3). \qquad (5.43)$$

LITERATURE

The Technology of Catalysts/Ed. by Mukhlyonov, I. P., Leningrad, 1974.

Instructions to the Laboratory Work "Analysis of Secondary Structure of Porous Solids by Mercury Porometry"

Low-Pressure Porosimeter

1. Make sure that the experimental setup is airtight.
2. Make sure that all cocks in the system are positioned correctly.
3. Do not connect the working roughing-down pump to the system under atmospheric pressure too fast, lest oil be ejected and spoiled.
4. Start the water cooling before switching on the diffusion pump.
5. When using mercury pressure gauges, do not allow the mercury to be ejected from the legs of the gauge.
6. Only persons instructed in safety rules and having passed the test are allowed to work with devices using metallic mercury.
7. Shut down the system in the following sequence: (a) close all cocks; (b) switch off the diffusion pump; (c) to switch off the roughing-down pump, set the cock on the line through which the pump communicates with the system to the neutral position, then switch off the pump, and let in the atmospheric air by turning the cock. When the cock is in the "off" position, the line must communicate with the atmosphere.

High-Pressure Porosimeter

1. Before the experiment, check: (a) the earthing of the porosimeter, and (b) the connection of the nitrogen bottle.

2. When opening the nitrogen bottle, first turn off the valve, then open the "nitrogen" cock on the porosimeter.

3. Feed nitrogen from the bottle only through a pressure regulator.

4. Make sure that the electric cables have rubber or PVC sheaths.

5. Switch off the high-pressure porosimeter in the following sequence: (a) press the "stop" button to cut off the oil supply into the bomb; (b) reduce the bomb pressure by slightly turning the "oil drain" cock counterclockwise and watch the pressure coming down with the aid of the high-pressure gauge; (c) as soon as the pressure in the bomb is normal, remove the cap and disconnect the electric circuit from the bomb plug; (d) turn off the main and locking nuts, then remove the plug together with the dilatometer from the bomb; and (e) clean the dilatometer from oil and withdraw the mercury together with the sample from it.

C. DETERMINATION OF SPECIFIC SURFACE
BY THE LOW-TEMPERATURE NITROGEN SORPTION METHOD

Experimental Setup and Procedure

The specific surface is determined by the adsorption method using a vacuum system illustrated in Fig. 115. Connected to the vacuum line via ground-glass joints are twelve cells *2* each having a capacity
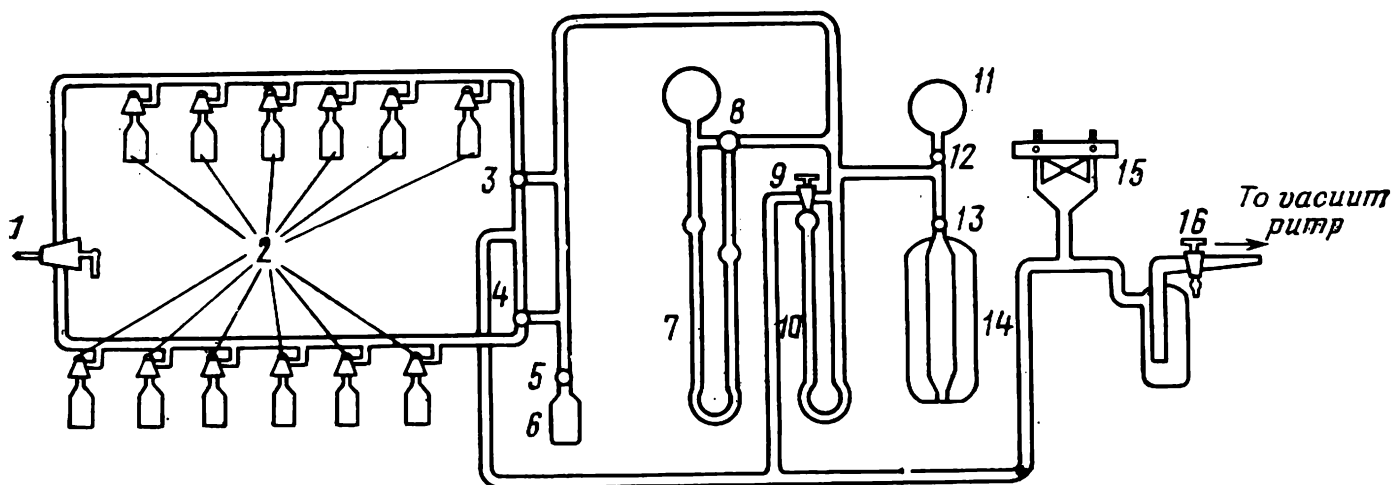
Fig. 115. Adsorption system

of 60 to 70 cm³ and admitting a sample. By turning a cell with its ground-glass joint about its axis, one can disconnect it from the rest of the system. A graduated 200-cm³ flask *14* is intended to measure the volumes of various parts of the system and is disconnected from the system by a cock *13*. The mercury pressure gauge *10* associated with the system through a cock *9* serves to measure the pressure in the system, while the oil (grade P-1 or BM-4) pressure gauge *7* with a cock *8* permits measuring pressure in the course of adsorption. The function of cocks *3* and *4* is to separately connect the lines with the

cells to the pump and to the measuring system. The system is evac-
uated by the roughing-down pump connected to it, with the cock *16*
open. The vacuum is monitored by a thermocouple vacuum gauge *15*
of the BT-2 type. The system is filled with nitrogen and the cells with
air (during replacement of samples) through a cock *1*. Nitrogen is
stored in a Dewar flask *11* with a cock *12*; the cell *6* filled with a sor-
bent and having a cock *5* can be used to increase the vacuum. Cylin-
drical ovens equal in number to the cells are intended to heat the latter
for deaeration of the powdered samples, the heating coils of the ovens
being connected in series. Before proceeding to measurement of the
sample surface, the system must be tested for air-tightness, the
cells must be calibrated, and the cell cooling coefficient must be de-
termined as a function of the sample weight.

The system is tested for air-tightness by means of a vacuum pump
with the cocks *3* and *1* closed; the system is evacuated to a residual pres-
sure of 1.33 Pa (when working with the cells of the first line, for the
second line of cells, the cocks *1* and *4* are closed). After both legs of the
oil and mercury pressure gauges have been made to communicate,
by means of cocks *9* and *8*, with the vacuum line, the system is tested
for air-tightness for 20 to 30 minutes. After the test, the Dewar flask *11*
must be filled with nitrogen. For this purpose, the end of the rubber
hose fitted on the cock *1* is immersed into the vessel with liquid nitrogen,
the cock *1* is slightly opened, and the air in the hose is driven by nitro-
gen into the system; the cock *1* is then closed, the system is evacuated
to about 1.33 Pa, the pump is switched off, the cock *16* is shut, and the
system is filled with nitrogen to atmospheric pressure through the
cock *1*. The cock *12* is closed.

For calibration of the cells (first line), they are made to communi-
cate with the vacuum line by the cock *4*; then, all cells (except one)
are disconnected from the system by means of the ground-glass joints,
and the excess nitrogen is pumped out of the system to a pressure of
1.33 Pa. One of the legs of the mercury pressure gauge *10* is discon-
nected by the cock *9*. The cock *12* is opened to supply nitrogen from
the Dewar flask *11* into the system till the pressure in the latter becomes
$P_1 = 1.6 \cdot 10^4$ Pa. The cock *13* is closed, the cock *9* is turned to estab-
lish communication between both legs of the mercury pressure gauge,
and the system is evacuated to the prescribed level; the pump is cut
off, the cock *16* is closed, both legs of the mercury gauge are made to
communicate, nitrogen is transferred from the flask *14* into the system,
and the pressure P_2 is measured. The measured pressure and the known
volume v_1 of the flask enable calculation of the system volume v_{ad}
in which the adsorption will take place:

$$v_1 P_1 = v_{ad} P_2, \quad v_{ad} = v_1 P_1 / P_2. \tag{5.44}$$

The volumes for all other cells are determined in a similar fashion.
Calibration of the differential pressure gauge with reference to

the mercury one boils down to determination of the ratio between the differences in the readings of each pressure gauge. This ratio serves as a factor of conversion from oil to mercury.

To determine the cooling coefficient, each cell is charged with a weighed amount of glass beads or rods (from 0.5 to 20 g). Different weighed amounts are taken to establish the effect of weight on the cooling action. The system is evacuated, and nitrogen is pumped in to a pressure of $1.6 \cdot 10^4$ Pa (first, the mercury pressure gauge is set to the working position, and nitrogen is fed to $P = 1.27 \cdot 10^4$ Pa; both legs of the oil pressure gauge communicate with the system). Then, the oil pressure gauge is set to the working position, and more nitrogen is added at $P = 0.33 \cdot 10^4$ Pa, that is the total pressure in the system amounts to $1.6 \cdot 10^4$ Pa. Next, all cells, except one, are evacuated. The pressure indicated by both gauges is recorded, and the cell is immersed into liquid nitrogen. After the levels in the pressure gauges have stabilized, their readings are taken once more. The values of the cooling coefficient A are derived from the formula

$$A = \Delta P / P, \tag{5.45}$$

where P is the nitrogen pressure in the system, in mm Hg, and ΔP is the gas pressure variation after the cell has been immersed into liquid nitrogen, in Pa.

Such measurements are taken for each cell, and the cooling coefficient A is plotted versus sample weight.

In measuring the specific surface of a sample taken in an amount (0.5 to 5.0 g) depending on the expected specific surface value (in the case of a finely porous material, a smaller sample is taken), the samples are placed in cells after being weighed on an analytical balance. The cells are turned on their ground-glass joints to communicate with the system and evacuated with heating up to 200-250°C. The cells are heated by the cylindrical electric ovens having their heating coils arranged in series. After the specified vacuum has been reached, both the evacuation and heating are discontinued. Nitrogen is supplied from the Dewar flask *11* (Fig. 115). into the cooled system (in the same sequence as during determination of the cooling coefficient) to $P = 1.6 \cdot 10^4$ Pa. All cells, except one, are turned on their ground-glass joints to be disconnected from the system, and the pressure gauge readings are taken; the remaining cell is immersed into the vessel with liquid nitrogen, and the oil pressure gauge is read out after stabilization of its level. Similarly, the rest of the cells are measured one by one. The specific surface is calculated using the formula

$$S_{sp} = B \, (\Delta P_{eq} - AP_{eq})/ag, \tag{5.46}$$

where B is the invariable part of the system volume;

$$B = 4.4 \frac{v_{ad} L}{(1 + t/273) \, 760} \; ; \tag{5.47}$$

P_{eq} is the equilibrium nitrogen pressure in the system, in Pa; ΔP_{eq} is decrease in the system gas pressure as a result of adsorption, in Pa; A is a factor of correction for the cooling effect, calculated from Eq. (4.45); L is a factor of conversion from the oil to mercury pressure gauge (ca. 0.07); 4.4 is the surface covered by 1 cm³ of gaseous nitrogen (under normal conditions), in m²/cm³; v_{ad} is the volume of the system in which adsorption takes place, in cm³, calculated from Eq. (5.44); q is the sample weight, in g; t is the ambient temperature, in °C; and a is a quantity determined by the ratio of the adsorbed nitrogen volume to the volume occupied by the adsorbed monomolecular layer:

$$a = \frac{v}{v_m} = \frac{240 P_{eq}/P_0}{(1 + P_{eq}/P_0)\,[1 + (240 - 1)\,P_{eq}/P_0]}, \qquad (5.48)$$

where P_0 is the pressure of saturated nitrogen vapours at 760 mm Hg and $-196°C$; P_{eq} is the pressure of nitrogen vapours at equilibrium with the absorbed layer; 240 is a constant representing the relative sorption capacity of the porous material—its value is practically the same for various adsorbents; v is the volume of adsorbed nitrogen under normal conditions; and v_m is the nitrogen volume corresponding to formation of the monomolecular layer.

The data involved in the determination of the specific surface calculated from Eq. (5.46) are entered in the following table:

Sample number	Sample weight, g	Specific surface, g/m²

LITERATURE

Ioffe, I. I. and Pismen, P. M., *The Engineering Chemistry of Heterogeneous Catalysis*, Leningrad, 1971.

The Technology of Catalysts/Mukhlyonov, I. P., Dobkina, E. I., Deryuzhkina, V. I. *et al.*, Leningrad, 1974.

Instructions to the Laboratory Work "Determination of Specific Surface by the Low-Temperature Nitrogen Sorption Method"

1. Before the experiment, test the system for air-tightness.

2. Make sure that both legs of the oil and mercury pressure gauges communicate with the system.

3. Before switching on the roughing-down pump, set the cock on the line through which the pump communicates with the system to the neutral position. To avoid contamination of the oil, do not switch on the pump if the line communicates with the atmosphere.

4. When working with oil and mercury pressure gauges, avoid ejection of oil and mercury from them.

5. Do not allow contact between Dewar flasks and oils or greases **to avoid explosions.**

6. Each time the Dewar flask has to be filled with liquid nitrogen, check it for integrity and proper condition (absence of cracks and scratches on the outside, moisture and dirt on the inner walls).

7. When a cell is immersed into the Dewar flask, avoid contact between their walls to rule out breakage.

8. After the experiment, equalize the pressure in both legs of the pressure gauges.

9. To switch on the vacuum pump, set the cock *16* to the neutral position, switch on the pump, and turn the cock to establish communication between the system and pump. During operation, the cock must be in a position allowing communication with the atmosphere.

D. DETERMINATION OF SPECIFIC SURFACE IN A CHROMATOGRAPHIC SYSTEM

Chromatographs of various types have found broad application in experiments and monitoring of industrial processes (see **Work 37**). In particular, they are employed to determine the specific surface **of** finelly divided porous materials, especially sorbents and catalysts.

Experimental Setup and Procedure

Figure 116 shows schematically a setup for determining the specific surface of finely divided porous materials by the chromatographic method. The main components of the setup are a chromatographic
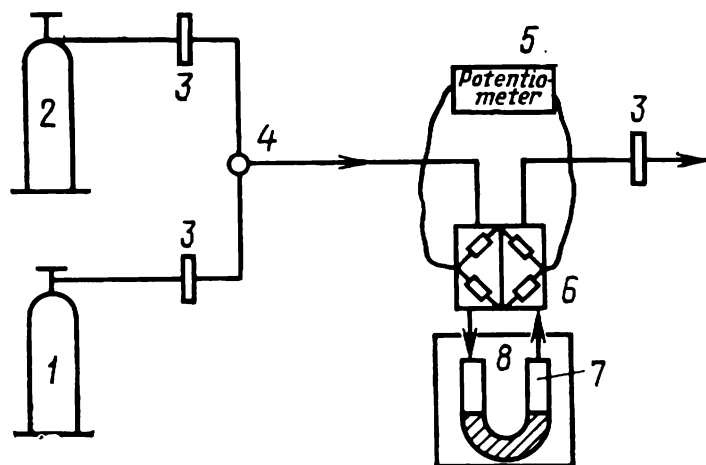

Fig. 116. Chromatographic system

column (tube with the test sample), a detector with two cells, and a recording potentiometer. Nitrogen is used as the sorbed gas, while the carrier gas is hydrogen whose sorption on the sample surface is virtually nil.

Before mixing, contaminants and water vapours are removed from the gases by passing them through special columns packed with

calcium chloride and charcoal. Trace amounts of oxygen are removed from nitrogen by passing the latter through a heated tube with copper filings. Nitrogen and hydrogen from the bottles *1* and *2* are fed through rheometers *3* into a mixer *4* from which the gas mixture flows into the reference cell of the detector *6*, then into the tube *7* with the sample. Having passed through the sample, the gases enter the flow cell of the detector *6* and are vented into the atmosphere through a rheometer *3*. The detector *6* incorporates a Wheatstone bridge, the resistance of its arms depending on the composition of the incoming gas. The detector output is recorded by the potentiometer *5* on a chart strip. If the gas composition in the reference and flow cells is constant, the pointer of the potentiometer is stationary, and this

Fig. 117. Chromatogram

position of the pointer is arbitrarily taken as the zero position. When the tube *7* with the sample is immersed into the Dewar flask *8*, the nitrogen in the nitrogen-hydrogen mixture entering the tube is partially adsorbed on the sample surface. The adsorption continues till the entire sample surface is enveloped with nitrogen. In the course of adsorption, the composition of the gas entering the flow cell of the detector will differ from that of the gas in the reference cell. This change in composition will alter the resistance of the right arm of the Wheatstone bridge, and the potentiometer *5* will register an adsorption peak *1* (Fig. 117). As soon as equilibrium is established in the solid-gas system, the gas concentrations in the detector cells will become equal, and the recorder will draw a straight line.

After the Dewar flask is removed, the nitrogen adsorbed on the sample surface will start being desorbed into the continuously flowing gas, then the composition of the gas entering the reference and flow cells will change again for a short period of time, and the chromatogram will feature a desorption peak *2*. The area of the adsorption peak on the chromatogram is proportional to the amount of adsorbed nitrogen, the areas of both adsorption and desorption peaks being equal. However, the adsorption peak is diffuse as a rule, which makes it difficult to measure its area, therefore, the area of the more clearly defined desorption peak is usually measured. The formation of a monomolecular nitrogen layer on the sample surface is ensured by selecting appropriate ratios of the gases in the initial mixture. The partial nitrogen pressure in the gas mixture must range from 1/10 to 1/20. If it exceeds 1/10 a polymolecular layer is formed, and the calculation results will be excessively high. If the partial pressure

is less than 1/20, the sample surface is covered by nitrogen molecules but partially.

When the system is switched on, the prescribed hydrogen and nitrogen flow rates are preset by means of coarse and fine pressure regulators. The oven for purging oxygen from nitrogen is energized, and 10 to 15 minutes must pass before the tube with copper filings becomes properly heated. Next, the chromatograph is switched on, and the filament current is adjusted. The gas line is blown with air for 15 to 20 minutes, the recorder pen is set to zero, and the experiment is started.

To calibrate the instrument, the necessary amount of nitrogen is drawn with a syringe. The chart strip drive of the recorder is energized, the syringe needle is inserted into the hole of a special calibrating device, and the nitrogen is injected into the gas mixture by pushing the syringe piston. The area of the peak appearing on the chromatogram is measured. Every measurement is taken at least three times. The calibration factor depends on the speed of the chart strip and the scale of the potentiometer input signal. With the chart strip moving at a speed of 60 mm/min and the input scale being 1 : 1, the calibration factor equals 0.023 cm^3/cm^2.

To measure the specific surface, a sample is weighed on an analytical balance and inserted into the tube 7 (Fig. 116). The tube with the sample is placed in the oven for activation of the sample surface. At the same time, nitrogen is passed through the sample. While this is being done, the tube is connected to the lower part of a four-way cock. When this cock is turned through 90°, the tube with the sample is blown with the gas mixture for 10 to 15 minutes. Meanwhile, the tube is slowly immersed into the Dewar flask, making sure that the nitrogen does not splash and that the bubbles of the foam in the bubble flow meter move upward. After the appearance of the adsorption peak on the chromatogram and return of the recorder pen to the initial position, the Dewar flask is quickly removed. At the same time nitrogen is desorbed from the sample surface. To accelerate the desorption (to have a sharper peak), the tube with the sample can be heated by water at room temperature.

After the desorption is over, the area of the desorption peak is measured. If the area is small, it must be increased by the scale knob of the chromatograph in repeated experiments with the same sample, which also improves the area measurement accuracy.

The chart strip of the recorder is stopped, and the potentiometer itself is switched off. The filament current is reduced, and the chromatograph is de-energized. Also de-energized are the sample cleaning and activation ovens. At first the pressure regulators on the bottles, then the fine pressure regulators, are closed.

The calculation in which the adsorption peak area is multiplied by the calibration factor gives the amount of nitrogen adsorbed on

the sample surface. The surface occupied by this amount of nitrogen. is calculated assuming that the area of a nitrogen molecule in the dense monomolecular layer is 16 Å. The specific surface S_{sp} is calculated from the formula

$$S_{sp} = S_{peak} K \frac{6.02 \cdot 10^{23}}{l \cdot 1000 \cdot 22.4} 16 \cdot 10^{-20} \frac{1}{g} , \qquad (5.49)$$

where S_{peak} is the peak area, in cm²; K is the calibration factor, in cm³/cm²; g is the sample weight, in g; and l is the scale factor.

At $K = 0.023$ cm³/cm², we have

$$S_{sp} = 0.1 S_{peak}/gl. \qquad (5.50)$$

Eq. (5.50) holds under the following conditions: $G_{mix}/G_N = 10\text{-}20$ and a chart strip speed of 10 mm/min. Thus, to calculate the specific surface, one must determine the sample weight, scale factor, and desorption peak area.

LITERATURE

Ioffe, I. I. and Pismen, P. M., *The Engineering Chemistry of Heterogeneous Catalysis*, Leningrad, 1971.

The Technology of Catalysts, Mukhlyonov, I. P., Dobkina, E. I., Deryuzhkina, V. I. *et al.*, Leningrad, 1974.

Instructions to the Laboratory Work "Determination of Specific Surface in a Chromatographic System"

1. Before the experiment, test the system for air-tightness.

2. When working with gas bottles, make sure that they are always capped when not in use.

3. When working with gas bottles, first open the pressure regulator, then carefully turn the discharge valve, making sure that the gas flows out at a particular pressure. The bottles must be protected against heating.

4. Do not allow Dewar flasks to be even in the slightest contact with oils or greases to avoid an explosion. Each time the Dewar flask is filled with liquid nitrogen, check its condition. Do not use damaged flasks. There must be no moisture or contaminants on the surface of the glass vessel.

5. When immersing the tube with the sample into liquid nitrogen, make sure that the tube does not touch the walls of the Dewar flask to avoid breakage of both.

LABORATORY WORK 33. ANALYSIS OF SORBENT AND CATALYST STRUCTURE BY ELECTRON MICROSCOPY

For a more complete picture of the porous structure of sorbents and catalysts, one must not only know its quantitative characteristics, but also have an idea of the surface topography and morphology. The latter two can be visualized by direct observation of the internal surface of a sorbent or catalyst specimen. Since the commonly used solid granular catalysts and sorbents have a developed surface, the

size of the particles making up a grain and forming this surface ranges from several angstroms to several micrometres. This structure can be observed with the aid of an electron microscope in which magnified images of the specimens are constructed by electron beams.

The basic optical train of an electron microscope (Fig. 118) differs from that of the ordinary light microscope in that all light optical components are replaced by the corresponding electronic ones, that is the light source is replaced by a source of electrons, and glass lenses are replaced by electromagnetic ones.

An electron microscope comprises the following basic components: column, vacuum system, and power supply with control panel. The column accommodates all of the lenses, the fluorescent screen, and the camera. The image in an electron microscope is built up as a result of dissimilar scattering of electrons. As they pass through an object, electrons scatter to the greater extent, the higher the atomic number of the element of the particles and the greater the thickness of the object. The electrons scattered beyond a particular small angle are absorbed by the aperture diaphragm and do not take part in image formation. Therefore, particles of an element having a low atomic number (e.g., carbon) will produce a low-contrast image on the microscope screen, while those of an element with a high atomic number (e.g., platinum) will produce a high-contrast image. If the specimen is a combination of amorphous particles of the same composition, the image contrast is indicative of their relative thickness. Thicker portions appear darker than the thinner ones. In this case, the object must be sufficiently thin (100 to 400 Å). Otherwise, it will become heated considerably as a result of electron absorption and may

Fig. 118. Optical train of an electron microscope

1—electron gun; *2*—condenser lens; *3*—object; *4*—objective lens; *5*—intermediate lens; *6*—projection lens; *7*—image screen

eventually be destroyed. Hence, the main difficulty in examining catalysts by electron microscopy is the preparation of the specimen which must be extremely thin.
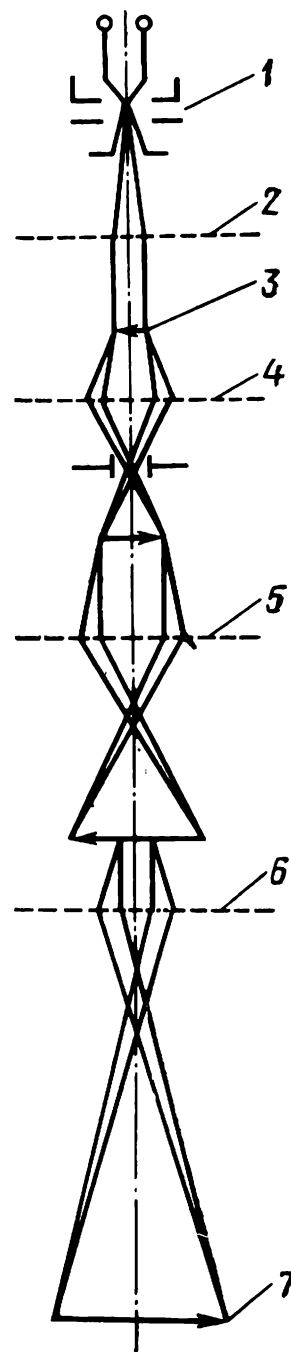
Experimental Procedure

One of the preparation techniques involves making a suspension or a powder. It includes the following basic steps: (1) preparation of supporting films; (2) dispersion of specimens; and (3) preparation of specimens.

The supporting films in electron microscopy perform the same function as slides in optical microscopy. Therefore, they must meet the following requirements: supporting films must be "transparent" to electrons, that is exhibit a low scattering power; their structure must not veil that of the object observed in the electron microscope; and they must be mechanically strong, thermally stable, and not chargeable by the electron beam. There are several types of films: plastic, carbon, metallic, quartz, and so on.

The carbon, quartz and metallic supporting films are prepared in a special spraying apparatus. Plastic films are easier to make. For example, to prepare a collodion support, a drop of a 1% solution of collodion in amyl acetate is introduced into a crystallizer with distilled water, whose evaporation results in a smooth film of uniform thickness, applicable on grids. On the supporting film carried on a grid is applied a suspension or powder of the specimen. The suspension is applied by means of a metal loop with a diameter equal to that of the grid, while the powder is applied by a soft brush.

When bulky specimens "opaque" to the electron beam are used, the indirect technique of making replicas is involved. This approach resides in examination not of the object itself, but the replica of its surface. Replicas may differ both in the material they are made of and in the way they are prepared. Of all the multitude of the existing replicas, the most commonly used at present are carbon (one- and two-stage) and plastic (collodion, Formvar) ones. Replica preparation techniques differ in that carbon replicas are prepared by vacuum evaporation, while the plastic ones involve application of a solution of a particular composition on the specimen surface. The replicas prepared by vacuum evaporation can be either applied directly on the surface of interest or on a negative replica, which makes them one- or two-stage.

Carbon replicas are produced in a vacuum evaporation unit (Fig. 119). Carbon evaporates as a result of direct contact between carbon electrodes in a vacuum of 10^{-4} mm Hg. The thickness of the deposited film is monitored with reference to the colour of an aluminium foil piece placed next to the specimen. The carbon film 100 to 200 Å thick on the foil is reddish brown in colour. After the film has been deposited, the specimen is immersed into a solvent which dissolves the specimen but does not affect the film. The film is detached from the specimen, washed in water, transferred onto a grid, dried on filter paper, and examined in the electron microscope.

If the specimen dissolves poorly or not at all, or if the surface of interest must be preserved, the replica is detached from the specimen mechanically, with the aid of a thick layer of gelatin. For this purpose, a 30-40% solution of gelatin in water (45-50°C) is prepared and applied in a uniform and relatively thin layer on the non-contact side of the replica which is still on the specimen, and the gelatin is allowed to dry. After it has dried completely (about 2 hours), the gelatin is carefully removed together with the carbon film by means of a razor and placed in warm distilled water with the gelatin down. The water is slowly heated to 80-90 °C. After dissolution of the gelatin, the free carbon film rises up to the water surface. It is washed twice in hot distilled water, then in alcohol, transferred onto a grid, dried, and inserted into the electron microscope for examination.

Fig. 119. Carbon replica spraying apparatus

1—vacuum bell jar; *2*—carbon electrodes; *3*—specimen (*θ*—carbon or metal spraying angle); *4*—table with controlled tilt

If another replica must be taken from the ¡specimen, it is recommended first to clean the surface of interest with gelatin. To this end, hot gelatin is applied on the specimen, and, after it has dried, peeled off and thrown away. The surface cleaned in this manner is ready for further analysis.

For the surface relief to be reproduced in the best way, the replica must be as thin as possible. To add contrast, replicas are shadowed. This is done by spraying a thin layer (ca. 6-9 Å) of a heavy metal (Pt, Ir, Cr) on the specimen surface in vacuum. The shadowing is done at angles ranging from 10 to 45° depending on the surface relief; the more pronounced the relief, the greater the variety of slopes of the surface details, hence, the greater the angle of shadowing. After shadowing, a carbon film is deposited on the surface at a right angle (Fig. 120*a*, *b*).

Figure 120*c* shows self-shadowing of carbon replicas. Carbon is deposited on the specimen not at a right angle as in the case of carbon replicas preshadowed with a metal, but obliquely. In this case, the greatest amount of carbon is deposited on the sides facing the shadowing source, while the shadowed sides receive the least amount. Owing to the fact that carbon particles rebound from the walls of the vacuum bell jar and the capacity of carbon to partially migrate over the surface, it is also deposited in the shadows thrown by the surface irregularities. Thus, when carbon is deposited on the specimen surface obliquely, there is not a single part of the surface that is not covered by the carbon film, and a continuous replica is formed having different thicknesses in different parts of the surface relief. This
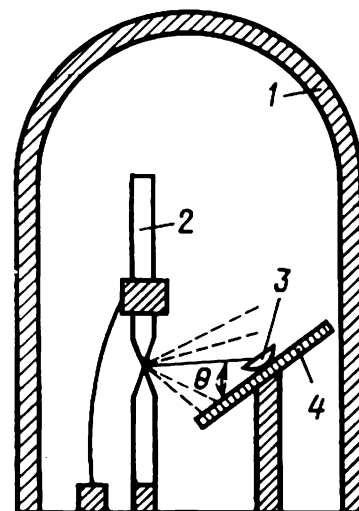
difference is precisely what enhances the image contrast:

Prepared specimens are examined in the electron microscope. Examination of powders allows determining the size and shape of particles and their size distribution. Studies into grain topography, determination of the structural uniformity and mutual arrangement of particles in the structure call for examination in the electron microscope of a replica taken from the section of a catalyst or sorbent grain. If the grain structure is not uniform, it takes more photographs to determine the average grain particle size and the specific surface (the number of photographs depends on the degree of grain non-uniformity and the spread of particle sizes). The specific surface is determined by electron microscopy from the formula

$$s = \frac{K}{\rho} \frac{\sum n d_p^2}{\sum n d_p^3}, \qquad (5.51)$$

where K is the form factor, ρ is the true density, n is the number of particles, and d_p is the mean diameter of particle projections. If the particles are round, the following formula can be used in the first approximation:

$$s = 6/\rho \bar{d}_p. \qquad (5.52)$$

Fig. 120. Preparation of a carbon replica preshadowed with metal (a, b) and self-shadowed (c)
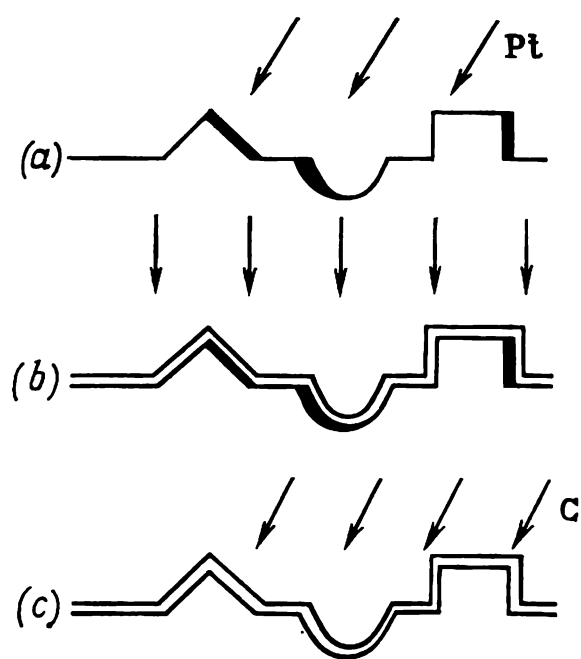
Apart from the difference in size of the particles making up the grain structure, different phases may be present in the catalyst or sorbent. Examination of specimens prepared under conditions of varying process parameters gives an insight into the formation and development of these phases and reveals their arrangement and number.

The analysis data must be tabulated as follows:

Specimen number	Specimen name	Mean particle diameter d_p, Å	Specific surface s, m²/g	Description of photographs	
				topography	morphology

LITERATURE

Ilmenev, E. S. and Pavlov, E. G., *A Guide to Electron Microscopy*, Moscow, 1970.

Pilyankevich, A. N., *Transmission Electron Microscopy*, Kiev, 1975.

Instructions to the Laboratory Work "Analysis of Sorbent and Catalyst Structure by Electron Microscopy"

1. Select the catalyst specimen preparation technique.

2. Prepare a specimen (suspension, powder, or replica, depending on the object of examination).

3. Insert the specimen into the microscope, select the specimen area to be photographed, take photographs, develop the photographic plates, and print the pictures (at least 10 from each specimen).

4. Study the topography and morphology of the internal catalyst surface on the photographs. Evaluate the uniformity of the catalyst grain.

5. Determine the mean diameter $\bar{d_p}$, specific surface and shape of the particles making up the catalyst structure.

6. Switch on the electron microscope and work with it under the instructor's supervision. Use the operating manual supplied by the manufacturer with each model. Observe the rules for safe handling of high-voltage equipment.

LABORATORY WORK 34. THERMAL ANALYSIS

Thermal analysis gives an insight into many physical and industrial chemical processes involving liberation or absorption of heat. These include such physical processes as melting, boiling, sublimation and evaporation, polymorphic transformations, and transition from the amorphous to crystalline state, and such chemical reactions as dissociation and dehydration, reduction and oxidation, exchange and isomerization. One of the ways to study such processes and reactions is temperature measurement. This analysis technique is recommended for determining the phase composition of solid inorganic materials, defining the temperature range of catalyst existence, measuring heat capacity and thermal conductivity. The analysis boils down to studying the phase changes occurring in individual substances or complex systems with reference to the thermal effects accompanying these changes.

One of the most widely used instruments for measuring temperature variations remains the Kurnakov pyrometer comprising a photocamera, light sources, reflecting galvanometers, and a device for controlling the heating of the furnace. This instrument can also be used to measure viscosity and electric conductivity, linear and volumetric expansion, and other parameters. For thermogravimetric (TG) measurements are used instruments whose operating principle is based on photoelectric registration of changes in the weight of a heated sample.

Apart from the temperatures typical of a particular process, the currently used thermal analyzers known as derivatographs also measure changes in the weight of a heated sample (thermogravimetry),

the rate of weight variations (differential thermogravimetry), and changes in heat content. This is what makes derivatographs advantageous over pyrometers and thermogravimetric instruments, owing to the absolute identity of the analysis data, which enables exact comparison of the weight loss curves with those of heat content variations and elucidates the nature of phase changes. Derivatographic measurements produce plots of temperature difference (between the sample and reference) versus time.

This work shows how differential thermal analysis (DTA) can be used to determine the directions and amounts of changes in the enthalpy of chemical reactions and how stoichiometric calculations can be made from the results of thermogravimetric measurements.

Experimental Setup and Procedure

The Paulik-Paulik-Erdey derivatograph is shown schematically in Fig. 121. The basic components of the instrument include an electric furnace, a balance, galvanometers, light sources, and a drum with photographic paper.
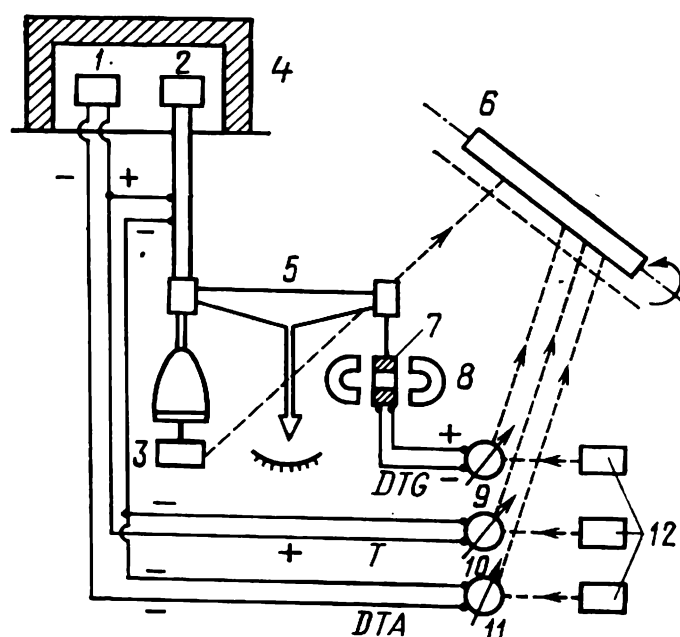
Fig. 121. Derivatograph

1, 2—platinum crucibles with reference and test samples; *3, 12*—light sources; *4*—furnace; *5*—balance; *6*—light-sensitive (paper; *7*—coil; *8*—magnet; *9, 10, 11*—galvanometers

A sample weighing 0.2 to 2 g is placed in a platinum crucible secured on the beam of the balance, then the sample is heated according to a set programme (at a rate of 2 to 10°C/min) together with the reference (alumina or magnesia calcined at a temperature above 1000°C). Changes in the sample weight are automatically recorded on the light-sensitive paper by the light source attached to the balance beam. The rate of weight variations is measured as follows. The field of magnetic forces induces current in the moving coil, whose voltage varies with the amount of deflection of the balance beam. The light signal of the galvanometer traces a TG or, to be more precise, DTG derivative on the paper rotating at a uniform speed. Another reflecting galvanometer is connected to the terminals of the thermocouple inside the sample, whose light signal traces a temperature (T) curve on the paper. A DTA curve is also traced.

Qualitative analysis of the derivatographic DTA curve involves establishment of the sign of enthalpy variation and determination of the characteristic temperatures corresponding to the maxima with subsequent comparison of the derived values with those published in the literature. The DTA curve gives unambiguously only the temperature of the extremum, whereas the points at which the phase change begins and ends can be defined only with a certain degree of accuracy.

Phase transitions involving sample weight variations are characterized by temperatures recorded on the DTA curve from which the boundaries of successive changes can be easily defined.

The results of this experiment are presented in the form of a derivatogram showing the extrema on the DTA curve, as well as calculation of the sample weight changes at each stage.

Figure 122 shows by way of example the derivatogram of a crystalline sample of aluminium hydroxide (pseudoboehmite), obtained under the following conditions: sample weight—200 mg; balance sensitivity—200 mg, DTA and DTG sensitivity—1/10 and 1/5; heating rate—5°C min.

The DTA curve of the aluminium hydroxide sample features two endothermic effects in the temperature ranges of 60 to 200 and 390 to 505°C with maxima at 135 and 460°C, respectively, and an exothermic effect in the temperature range of 240 to 390°C with an extremum at 300°C. The first endothermic effect corresponds to removal of adsorbed moisture, and the exothermic effect corresponds to crystallization of alumina. The second endothermic effect is due to the loss of structurally bound hydroxy groups with complete crystallization of alumina whose structure is ordered at 550 to 590°C.

Fig. 122. Derivatogram of a crystalline aluminium hydroxide sample

By projecting the corresponding points a, b, c, and d on the TG curves (a', b', c', d'), one can determine the weight variations associated with individual reactions with a high degree of accuracy.

Calculate the sample weight variations for each step of dehydration, using the TG curve. The H_2O losses are: 10 mg or 0.38 mole of H_2O per mole of Al_2O_3 over the $a'b'$ portion; 16 mg or 0.60 mole of H_2O per mole of Al_2O_3 over the $b'c'$ portion; and 20 mg or 0.76 mole of H_2O per mole of Al_2O_3 over the $c'd'$ portion. The total loss over the TG curve is 51 mg or 1.95 moles of H_2O per mole of Al_2O_3.

Hence, after the first step of dehydration, the sample weighs 190 mg, composition—$Al_2O_3 \cdot 1.57H_2O$; after the second step, 174 mg, composition — $Al_2O_3 \cdot 0.97H_2O$; and after the third step, 154 mg, composition $Al_2O_3 \cdot 0.21H_2O$.

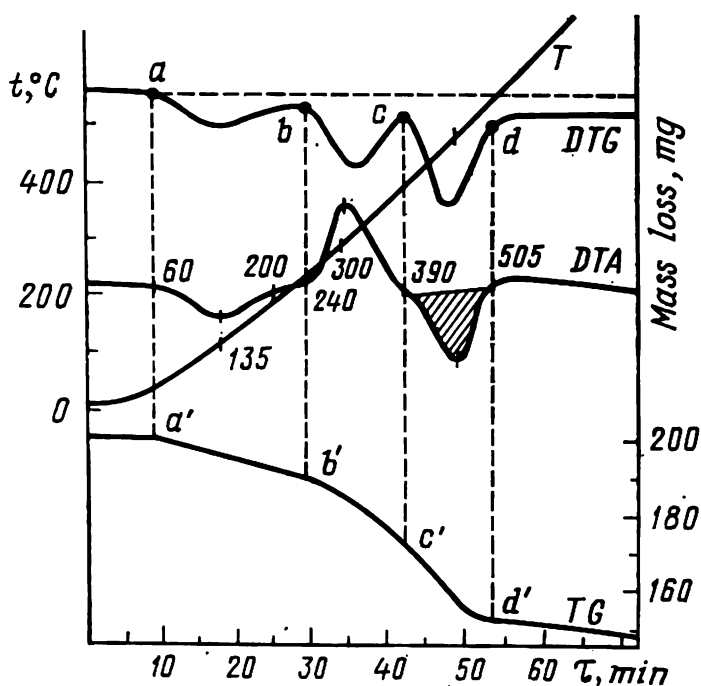The amount of enthalpy variation is determined from the DTA curve by

using the ratio of the areas confined by the maxima and the base line for the sample and reference. $CaCO_3$ is often used as the reference. To determine the area (hatched portion) the maximum is cut out and weighed on an analytical balance.

The conditions under which the derivatogram is taken, the calculation procedure and results are written on the back of the photographic paper with the experimental curves.

LITERATURE

Berg, L. G., *An Introduction to Thermography*, Moscow, 1969.

Instructions to the Laboratory Work "Termal Analysis"

1. Carry out the experiment under the instructor's supervision. Since derivatographs are made with the safety features built in, no additional safety precautions are to be taken.
2. Preset the sensitivity of the DTA and DTG galvanometers at 1/5 to 1/10.
3. Check the position of light signals.
4. Uncage the balance and preset its sensitivity at 100 to 500 mg.
5. Energize the heater, light sources (TG, DTG, T, DTA) and drive motors of the voltage regulator and control device.

LABORATORY WORK 35.
ANALYSIS OF SOLID MATERIALS
BY INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy is extensively used to evaluate the quality of raw materials and products of many industrial processes.

The broad application of this technique stems from the fact that some chemical bonds and groups of atoms produce absorption bands in the IR spectrum approximately at the same frequency irrespective of the molecule containing a particular bond or group.

IR spectra result from interaction between electromagnetic radiation and a substance, the beam energy being transformed to the energy of the particles.

The molecular energy can be divided, to a first approximation, into three additive components associated with: (a) rotation of a molecule as a whole, (b) vibration of the atoms forming the molecule, and (c) motion of electrons in the molecule. Placing a molecule in the field of IR radiation brings about changes only in its rotational and vibrational states. However, not all transitions between these levels are possible. In order to find out whether a transition is allowed or forbidden, one must look at the corresponding selection rule which is determined by the symmetry or spatial geometry of the nuclei constituting the molecule. A vibration is said to be active in the infrared spectrum if it brings about a change in the dipole moment of the molecule.

The main vibrational modes of bound atoms involve stretching and bending vibrations. The former represent periodic displacements of atoms along the A-B bond axis, require high energies for their excitation, and manifest themselves in the range of high frequencies. The bending vibrations changing the angles between bonds require less energy, hence, are observed in the spectrum at lower frequencies.

Any radiation is characterized by a wavelength λ (1 μm = 0.001 mm = 10^{-4} cm = 1000 nm = 10^4 Å) or by a wave number v, which represents the number of wavelengths per cm ($v = 1/\lambda$, where λ is expresssed in cm). The wave number v is expressed in cm^{-1}.

An absorption band in the IR spectrum (Fig. 123) is characterized by intensity I. The amount T (%) of infrared radiation transmitted by a substance is determined from the formula

Fig. 123. IR spectrum of potassium metavanadate

$$T = I/I_0 \cdot 100 \qquad (5.53)$$

where I_0 is the intensity of the incident radiation, and I is the intensity of the radiation passing through the absorbing medium.

Then, the amount A (%) of the infrared radiation absorbed by the substance is

$$A = 100 - T = \frac{I_0 - I}{I_0} \, 100. \qquad (5.54)$$

The extinction or optical density D of the substance is calculated using the equation

$$D = \log (I_0/I) = KCd, \qquad (5.55)$$

where K is the extinction coefficient, that is the absorptive power of the substance, d is the specimen thickness, and C is the concentration of the substance of interest in the specimen.

Thus, knowing the relationship between the optical properties of a substance and its mass, one can perform not only qualitative but also quantitative analysis of the specimens.

To obtain a qualitative IR spectrum of absorption requires that the size of the substance particles be, in the ideal case, smaller than the wavelength of the incident radiation, which mitigates the Christiansen effect arising as a result of the difference in the refractive indices of the surrounding medium and the solid particle.
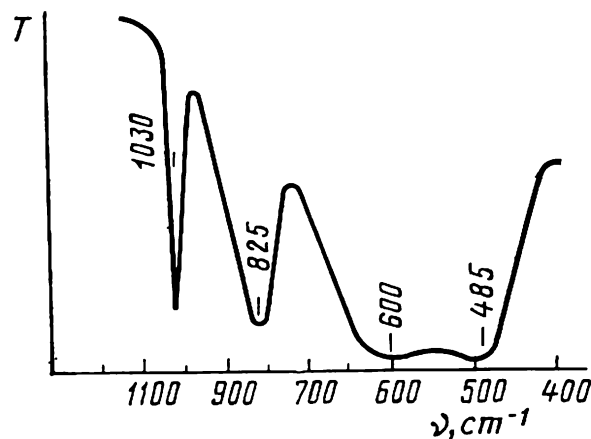
Experimental Setup and Procedure

The most commonly used instruments are double-beam spectro-photometers whose operation is based on what is known as the null method (Fig. 124). In the course of scanning, two light beams are alternately directed from the radiation source to the entrance slit of the monochromator, which pass through the specimen and reference cell, respectively. Both beams act alternately through a chopper on a detector in which a variable electric signal is formed if the beam energies are not equal. The signal is conditioned by an amplifier and a rectifier, then actuates the motors driving the photometric system
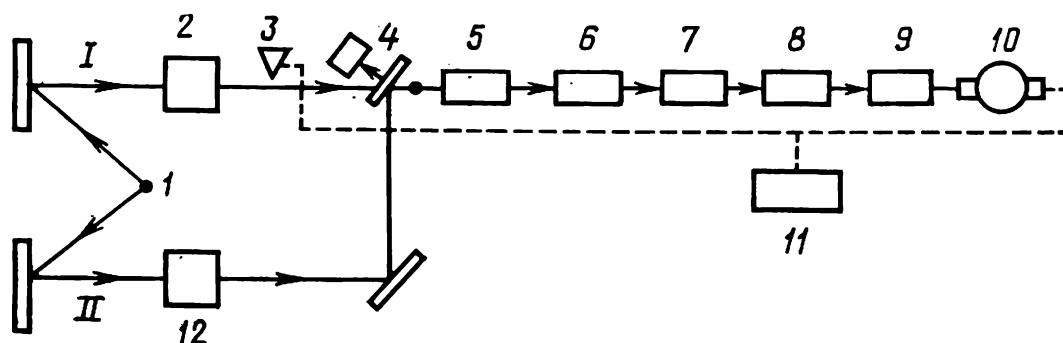
Fig. 124. Double-beam spectrophotometer

I, II—measurement and reference channels of IR radiation; *1*—IR source (globar or Nernst filament); *2, 12*—reference and specimen cells; *3*—compensating photometric wedge; *4*—chopper; *5*—monochromator; *6*—detector; *7*—signal amplifier; *8*—rectifier; *9, 10*—motors; *11*—recorder

(diaphragm, wedge); the wedge screens off the reference beam until its intensity becomes equal to that of the main beam, that is until the electric signal disappears. The photometric system is associated with the recorder pen and calibrated in percentage transmission or optical density.

The spectrum is recorded on a special paper strip as percentage transmission (from 0 to 100%). The automatic change-over of prisms with uninterrupted recording and the incessant air conditioning in the monochromator chamber rule out exposure of the NaCl and KBr prisms to moisture, whereby they are protected against damage. The experimental procedure is as follows.

1. The amplifier is switched on (amplifier unit, "amplifier" toggle switch). The indicating light must come on. The amplifier must be allowed to warm up for 15 minutes.

2. Water is supplied (at a rate of 1 dm³/min), and the radiation source is energized ("burner" toggle switch on the power supply).

3. The spectrophotometer is switched on ("spectrometer" switch on the monochromator unit). The chopper must start operating, and the indicating lights of the recorder and prism indicator must come on.

4. The specimen is inserted into the cell holder and introduced into the channel (if necessary, a cell with the reference is also introduced). The shutters of the light source are opened.

5. The operating mode is set: the "slit" knob is positioned at 6-8 mm; the spectrum scanning speed ("cm^{-1}/min") is set at 400; the pen speed ("s/0-100%") is set at 4; the paper strip feed ("mm/100 cm^{-1}") is set at 10; "gain" on the amplifier unit is set at 8 ("coarse") and at 3-6 ("fine").

6. The "variable wave number" toggle switch is set to the "on" position. The "fast speed" slider is moved to and fro to preset the wave number from which the spectrum must be recorded (with reference to the scale on the upper part of the instrument).

7. The pen, pinch, and paper bail roll are lowered.

8. The spectrum is recorded, after which the "variable wave number" toggle switch is positioned at "off". The pen and pinch are raised. The paper feed is switched off.

9. The light source shutters are closed. The spectrophotometer is switched off.

10. The amplifier is de-energized, the burner is switched off, and the water supply is cut off.

The specimens are prepared for analysis by the "suspension" method or by pelletizing with halides of alkali metals.

The "suspension" method resides in that the specimen is dissolved in an agate mortar together with oil (Nujol) for 10 to 15 minutes, then the resulting paste is distributed by a spatula along one of the ends of a salt plate. The other, overlying plate is slid over the first one evenly to spread the paste all over. With most compounds, the best results in the spectral region of 2 to 8 µm are provided by the ratio of 10 mg of the specimen to 2 drops (25 mg) of the oil, or 30 mg of the specimen to 2 drops of the oil in the region of 8 to 15 µm. This procedure normally gives layers containing about 1 mg/cm^2 of the specimen, which corresponds to a paste layer approximately 0.01 m thick.

The most suitable alkali metal halide for pelletizing is potassium bromide producing no absorption bands up to 28 µm. Small amounts (1 to 5 mg) of the substance are ground and mixed with the powder of the highly pure halide; the resulting mixture is charged into a mould and compressed with continuous evacuation into transparent pellets or discs. If the evacuation of the adsorbed air is not sufficient, the pellets tend to turn turbid after some time. The halide powders used for pelletizing must be dry, for which pourpose the finely divided potassium bromide powder is kept in a dry atmosphere (e.g., in a heated vacuum furnace); if KBr is kept in an exiccator, it must be regularly dried (at 100 to 400°C) to remove the adsorbed moisture. For best results the specimen must be thoroughly comminuted, the best and fastest way to do that being grinding it in vibratory mills.

This work includes several assignments for studying the chemical structure of solid-phase specimens (catalysts) by IR spectroscopy.

A. LOCATION OF THE MAXIMA
OF THE MAIN ABSORPTION BANDS IN THE SPECTRA
OF KNOWN COMPOUNDS

This assignment is aimed at determining the characteristic frequencies of atomic group absorption in the spectrum of a known compound in the range of 2000 to 400 cm^{-1}.

In this range, spectra are taken of known substances (carbonates, sulphates, nitrates, etc.). The experimentally found absorption frequencies are compared with the tabulated values of characteristic frequencies, and the substances are classified according to atomic groups.

The assignment is carried out in the following sequence.

1. The spectrophotometer is switched on and prepared for the experiment.

2. The appropriate formula is used to put down the atomic groups present in the compound under examination and the corresponding characteristic frequencies.

3. Next, the specimens are prepared for analysis. To this end, 20 mg of the substance are ground in a jasper mortar, a small (ca. 2 ml) amount of isopropyl alcohol is added, and the contents are carefully stirred (for at least 20 min). The suspension is then allowed to stand, a drop from the upper layer of the suspension is transferred (by the pestle) onto a polished potassium bromide plate so that it is evenly distributed over the crystal surface. After the liquid has evaporated, another drop is applied. (Make sure that large salt particles do not precipitate on the plate surface.) The transfer of drops is continued till the entire plate surface is covered by a sizable layer of the powder.

4. The plate is placed in the specimen holder in which it is inserted into the cell compartment or, to be more precise, fitted into the guide of the left channel *I*, and the spectrum of the salt is taken in the usual mode, in the range of 2000 to 650 cm^{-1}. Then, the most intense band is located in the spectrum, and the percentage transmission at the absorption maximum is determined. If it is 20 to 30%, the specimen is ready for analysis, otherwise, the salt plate is again placed on the specimen until the percentage transmission at the maximum of the selected intense band goes beyond 20-30%.

5. The spectrum is recorded with a potassium bromide plate being used as the reference (channel II).

The results are tabulated as follows:

Position of maxima of the absorption bands observed in the spectra, cm⁻¹	Reference data		Attribution of the experimentally observed frequencies to a particular atomic group
	Atomic group	Absorption bands corresponding to this atomic group, cm⁻¹	

The experimental values of the absorption bands are compared with the tabulated values of the characteristic frequencies of the corresponding atomic groups.

B. QUALITATIVE ANALYSIS OF A MIXTURE OF INORGANIC SALTS BY INFRARED SPECTRA

In this assignment, a salt mixture must be analyzed qualitatively on the basis of the absorption spectrum.

With the spectra of the substances that may be present in a given mixture and the characteristic frequencies of the atomic groups forming these compounds being available (assignment A), the experimental frequencies of the mixture spectrum (as well as the intensities) are compared with the characteristic frequencies, and the comparison results are indicative of the presence of particular anions in the mixture.

The assignment is carried out in the following sequence.

1. The spectrophotometer is switched on and prepared for the experiment.

2. The characteristic frequencies corresponding to the maxima of the absorption bands in the range of 2000 to 400 cm⁻¹ are tabulated as follows:

Position of experimentally observed absorption band maxima, cm⁻¹	Reference data	
	Atomic group	Absorption bands corresponding to this atomic group, cm⁻¹

3. Salt mixtures are prepared for analysis with the specimens being deposited from a suspension.

4. The spectrum is recorded with a potassium bromide plate being used as the reference. It is compared with the spectra of the references (individual salts), and the specimen composition is qualitatively determined.

C. DETERMINATION OF THE STRUCTURE
OF INORGANIC COMPOUNDS FROM INFRARED SPECTRA

This assignment is aimed at elucidating the structure of inorganic compounds from the number of absorption bands active in the IR spectrum.

The number of absorption bands active in the IR spectrum is determined by the selection rules based on concepts of symmetry. For example, the spectrum of a nitrate-anion group must feature three absorption bands in accordance with this theory. In nitrates of metals, the symmetry of this anion may be less pronounced as one passes from salts with a predominantly ionic nature of the metal-anion bond to those with a more covalent bond. A decline in the symmetry of the nitrate anion must be accompanied by an increase in the number of absorption bands active in the IR spectrum from three to six (Table 20).

Table 20

Anionic group	Point group	ν_1	ν_2	ν_3	ν_4	Number of bands
NO_3^-	D_{3h}	A_1' (IA*)	A_2 (A**)	E (A)	E (A)	3
$-ONO_2$	C_{2v}	A_1 (A)	B_1 (A)	A_1 (A)+ $+B_2$ (A)	A_1 (A)+ $+B_2$ (A)	6

* IA-vibration inactive in IR spectra.
** A — vibration active in IR spectra.

The assignment is carried out in the following sequence.

1. The spectrophotometer is switched on and prepared for the experiment.

2. Specimens of Na^+, K^+, Ca^{2+} and Zr^{4+} nitrates are prepared for analysis from a suspension.

3. The absorption spectra are taken in the range of 2000 to 650 cm^{-1}.

4. The number of the main bands is counted, and the bands are compared with the tabulated data. The structural form of the anion group in each salt is established and written down. The results are tabulated as follows:

Cation of the analyzed nitrate	Atomic group	Number of absorption bands typical of this group	Experimentally observed number of bands	Conclusion

LITERATURE

Kiselev, A. V. and Lygin, V. I. *Infrared Spectra of Surface Compounds and Adsorbed Substances*, Moscow, 1972.

Little, L., Supplement Chapters by Kiselev, A, Lygin, V., *Infrared Spectra of Adsorbed Species*, London, 1966.

Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*, New York, 1963.

Instructions to the Laboratory Work "Analysis of Solid Materials by Infrared Spectroscopy"

1. Prepare the spectrophotometer for analysis under the instructor's supervision. Use the manual supplied by the manufacturer with the model.

2. Make sure that the compartment accommodating the IR radiation source (globar) is water-cooled.

3. Make sure that the prism position corresponds to the colour of the indicating light in the IR spectrophotometer.

4. Do not stop the instrument with the prisms being changed over at fast speed.

LABORATORY WORK 36. GAS ANALYSIS

Analysis of gases is of paramount importance in some research activities and the monitoring of some industrial processes, because the basic process parameters are determined only by the gas analysis results. Gas analysis usually involves two main procedures: sampling and analysis of the sample. If a gas has not been sampled correctly, the subsequent analysis will yield wrong results. Inaccuracies in the determination of gas composition lead to serious errors distorting the overall picture of the course of a process and its conditions, to say nothing of their adverse effect on the process monitoring and control. The composition of gases can be determined quantitatively with the aid of gas analyzers. According to their operating principle, all gas analyzers are divided into chemical and physical ones.

In chemical gas analyzers, the determination is based on absorption of the components of a complex gas mixture by respective absorbents forming with them (separately with each component) stable chemical compounds, as well as on burning some components to CO_2 or H_2O.

Physical gas analyzers make use of the major physical properties of the component of interest (volume, thermal effect, density, viscosity, electrical, optical or acoustic properties, etc.), which differ considerably from the similar properties of other components of the gas mixture. Depending on the amount of a gas mixture sampled for analysis and the concentration of a particular component to be analyzed, distinction is made between macromethods (at least 100 cm^3 of gas), semimicromethods ($2\text{-}20 \text{ cm}^3$), and micromethods (1 cm^3 and less).

All gas analyzers may be manual or automatic. Continuously working gas analyzers with automatic recording of the analysis re-

sults ensure non-stop monitoring of industrial processes and the ambient air. In such instruments, sampling of gases, their subsequent analysis, and the continuous recording of the results are made possible by using an electromechanical or hydraulic drive, which enables a process to be monitored in line at its speed.

Such gas analyzers are normally used to determine the concentration, or its variations, of a gas which is a component of a binary or ternary mixture. In spite of the differences in design, the operating principle and many parts of such instruments have a lot in common.
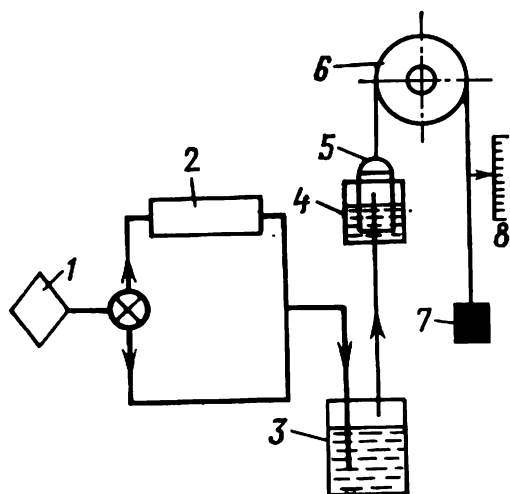
Fig. 125. Automatic gas analyzer
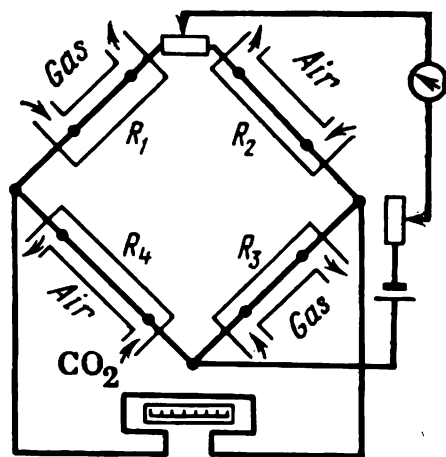
Fig. 126. Electric gas analyzer for determination of CO_2

Figure 125 shows schematically a *chemical* gas analyzer for determination of CO_2 or a CO and H_2 mixture. The operating cycle of such gas analyzers consists of suction (sampling) of the gas and its discharge.

The gas to be analyzed is periodically (once every two or three minutes) sucked in a certain amount (100 to 200 cm^3) into a volumeter *1*, passes through a distributor valve or combustion furnace *2* into an absorption vessel *3*, then into a measuring device (of the bell or float type) where the gas volume remaining after absorption is measured. The movement of the measuring element (bell *5* or float) traces, via a recording device *6*, *7*, and *8*, a dashed or solid curve on the chart, representing the variations in the composition of the gas mixture. Similar gas analyzers are used for analysis of flue or stack gases as well as lime kiln gases for content of carbon dioxide, carbon monoxide, hydrogen, and, in some cases, heavy hydrocarbons. Process gases are analyzed for content of ammonia, hydrogen chloride, chlorine, sulphur dioxide, oxygen, and hydrogen.

Widely applied in the industry are *electric* gas analyzers. The operation of such an instrument intended to determine a gas mixture component, such as carbon dioxide, is based on comparison of the thermal conductivity of air and the gas mixture containing carbon dioxide.

The resistance in electric gas analyzers determining carbon dioxide is measured by means of an unbalanced bridge circuit (Fig. 126) whose four arms have the same resistance. The bridge arms are made of thin platinum wires, two of which (R_2 and R_4) are inside air-filled chambers, while the other two (R_1 and R_3) are inside the chambers with the gas being analyzed. If both chambers contain the same gaseous medium, the thermal state of both wires and their temperatures will be the same because the conditions of their thermal equilibrium are similar. A change in the thermal equilibrium causes a proportional change in the resistance of one pair of arms, and the bridge balance is upset with the result that current is induced in the diagonal, the magnitude of this current being proportional to the change in resistance, that is to the amount of the liberated heat and, consequently, to the percentage content of carbon dioxide in the analyzed gas mixture. The same principle may underlie the operation of gas analyzers for determining the content of sulphur dioxide and other gas mixture components whose thermal conductivity differs widely from that of air.

Apart from analysis of flue gases, automatic electric gas analyzers can be used for determining the purity of hydrogen, nitrogen, and other gases, as well as for analysis of CO and CO_2 in a nitrogen-hydrogen mixture, ammonia downstream of the synthesis column, sulphur dioxide in kiln gases, oxygen and nitrogen in air liquefaction, some gases in the production of divinyl, methanol, ethanol, and other chemicals.

This work deals with analysis of gas mixtures by chemical gas analyzers.

Experimental Setup and Procedure

Gas analysis in a chemical laboratory is performed to monitor the processes of low- and high-temperature carbonization, pyrolysis, cracking and electrolysis and of NaCl solution, as well as an independent task. The approximate composition of the gas released during low-temperature carbonization of some fossil fuels is given in Table 21.

Table 21

Fossil fuels	Composition, vol.%						
	H_2	N_2	CO	CO_2	CH_4	C_nH_{2n}	H_2S
Lignites	5-23	2-17	4-9	3-34	21-59	1-8	8-10
Coals	11-20	3-25	3-11	7-14	46-63	1-5	1-7

Depending on the charge composition and process conditions, the composition of coke-oven gas varies approximately within the following limits (vol. %): hydrogen—50 to 62, methane—20 to 25, higher hydrocarbons—2.0 to 2.6, carbon dioxide—1.8 to 4.0, carbon monoxide—4.5 to 7.5, oxygen—0.2 to 0.5, and nitrogen—about 5. Complete analysis of a gas having the above or similar composition is carried out on gas analyzers of the ГХП-3 type (Fig. 127).
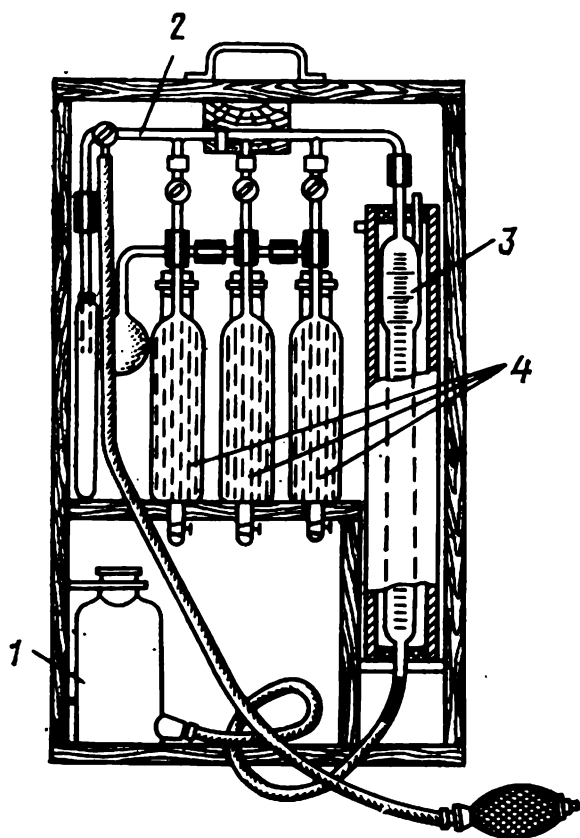
Fig. 127. ГХП-3 gas analyzer
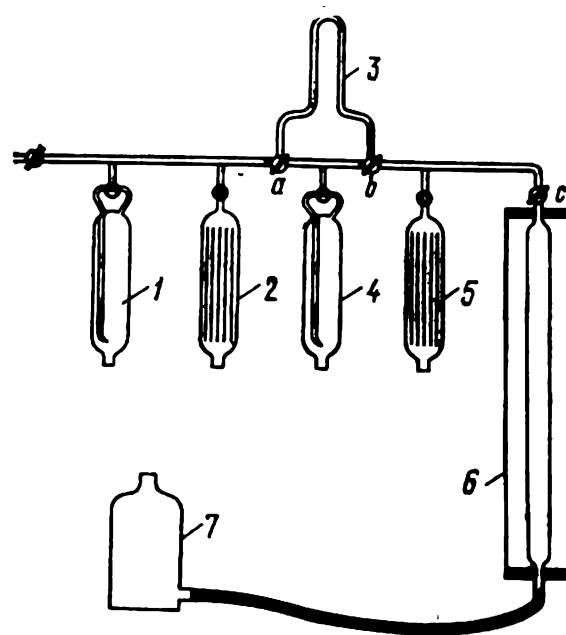
Fig. 128. ЛТИ gas analyzer

Such a gas analyzer comprises a 100-cm³ burette *3* whose lower part is graduated to read 0.2 cm³ (at a temperature of 20°C). The burette is placed in a cylinder filled with water. In addition, the instrument includes three absorption vessels *4* with solutions; the vessels are packed with glass tubules to increase the surface of contact between the absorbing solution and gas. The gas is distributed among the absorption vessels with the aid of a glass manifold *2* with cocks. There is also a levelling bottle *1* with a liquid seal to equalize the pressure in the burette, as well as for gas intake and displacement. The bottle is filled with a saturated NaCl solution or a 5% solution of H_2SO_4.

A gas analyzer of the ЛТИ type (Fig. 128) consists of a long measuring burette having a capacity of 100 cm³ and graduated to read 0.2 cm³, a manifold with five lower and two upper branch pipes and cocks *a*, *b*, and *c*, four absorption vessels *1*, *2*, *4*, and *5*, a quartz or metal loop *3* filled with cupric oxide, a levelling bottle *7*, and

a three-way cock ensuring communication of the device either with the atmosphere or with a gas holder. The absorption vessels *1* through *5* developed at the Leningrad Institute of Technology (ЛТИ) may be of two types: (a) including two cylinders arranged close to each other (the front cylinder being the working one, receiving the gas bubbled by a long capillary through a layer of the absorbing liquid, and the rear cylinder into which the liquid from the working cylinder is displaced), or (2) consisting of two glass cylinders, one placed into the other. The internal cylinder is made integral with a ground-glass stopper (or a rubber plug) through which both cylinders are joined together. To extend the surface of contact between the absorbent and gas, the vessels are packed with glass tubules. The device is intended for analysis of process gases by the method of absorption with separate complete combustion.

As the liquid seal filling the levelling bottle and measuring burette are, as a rule, used a 10% sulphuric acid or a NaCl solution, tinted with methyl orange, in which the solubility of the gases of interest is insignificant. The gas absorbents are as follows: 33% solution of KOH for absorption of CO_2 and H_2S in the vessel *5*; 20% KBr solution saturated with bromine for absorption of unsaturated hydrocarbons in the vessel *4*; alkaline solution of pyrogallol for absorption of oxygen in the vessel *2*; and ammoniacal solution of cuprous chloride Cu_2Cl_2 for absorption of carbon monoxide in the vessel *1*.

Preparation for Analysis. Before the experiment, all cocks and joints in the gas analyzers must be tested for air-tightness. When the levelling bottle is lowered, the levels of the reagents in the absorption vessels and the liquid seal in the burette must be constant. Next, all components of the analyzer are checked for cleanness (the manifold, measuring burette, and other glass parts must be clean from grease, absorbing solutions, etc.). The liquid in all absorption vessels and the measuring burette is brought up to the marks on the capillaries just below the cocks.

The loop with cupric oxide (II) is heated, and air is slowly passed at 400 to 500°C (5 to 10 cm³/min) from the measuring burette into the vessel with KOH through the loop. The oxidation of copper is continued till the volume of air in the measuring burette becomes invariable. If all of the oxygen (20.9 cm³ from 100 cm³ of the air in the burette) is spent for oxidation of copper, the remaining gas (nitrogen) is bled into the atmosphere, a new air sample is taken, and the oxidation is carried out in the same fashion to a constant volume. Thus, metallic copper transforms to CuO.

An amount of 100 cm³ of air is taken into the measuring burette, its oxygen (20.9%) being absorbed by the alkaline solution of pyrogallol. Then, the manifold is carefully purged with the remaining nitrogen, the cocks *a*, *b*, and *c* (Fig. 128) are turned to do the same with the loop containing cupric oxide, and the loop is disconnected

from the manifold. Now, both the loop and manifold are filled with nitrogen. The measuring burette is filled with the liquid seal up to the mark on the capillary. The gas analyzer is tested for air-tightness of all rubber joints and cocks.

Gas Sampling and Analysis. When the preparation of the analyzer is over, the three-way cock is turned to connect the measuring burette to the gas holder (the levelling bottle being raised up to the upper mark of the measuring burette), then the levelling bottle with the liquid seal is slowly lowered to displace the gas from the gas holder into the burette (100 cm^3). The gas in excess of 100 cm^3 is bled into the atmosphere through a port in the three-way cock, after which the measuring burette is disconnected from the atmosphere and gas holder by the three-way cock.

In determining the total content of CO_2 and H_2S, the gas is transferred into the vessel with the KOH solution and back into the measuring burette with the cocks of the vessel *5* and burette *6* (Fig. 128) open. This is done by slowly raising and lowering the levelling bottle. Such "pumping" is repeated six to eight times, then the level of the absorbing solution is brought up to the mark, the cock of the vessel is shut (but not that of the burette), and the volume of the remaining gas is measured with equal liquid levels in the measuring burette and levelling bottle. This procedure is repeated till the residual gas volume stops changing, after which the absorption of CO_2 and H_2S is considered to be complete.

The volume of CO_2 and H_2S (v_1) is calculated from the difference

$$v_1 = v_0 - v_2,$$

where v_0 is the volume of the gas sampled for analysis (usually 100 cm^3), and v_2 is the volume of the gas remaining after absorption of CO_2 and H_2S.

For absorption of unsaturated hydrocarbons, the gas is transferred into the vessel *4* with bromine water. The vessel is "pumped" five to six times, and the gas is transferred again, without measurement, into the vessel *5* with the KOH solution for absorption of the released bromine vapours (the washing is done till the brown bromine vapours disappear). Then, the gas is transferred into the vessel *2* with the alkaline solution of pyrogallol for oxygen absorption. Since oxygen is absorbed slowly, it normally takes at least 15 to 17 "pumpings" of the vessel. The first measurement should preferably be taken after the gas has been transferred ten times, then after fifteen transfers, and the absorption is completed only after two equal readings are taken. The absorption of CO with the ammoniacal solution of cuprous chloride Cu_2Cl_2 is also slow. The gas is usually "pumped" 14 to 16 times from the burette into the vessel *1* and back (to a constant volume).

When the experiment involves vessels provided with bubbling capillaries, the position of the cocks must be carefully watched. The painted end of a cock indicates that the gas is flowing through the capillary with the painted tip. If the painted end of the cock is turned up or down, the vessel is disconnected from the manifold. To transfer the gas into the vessel, the long capillary is used, while the short (right) one is used to transfer the gas from the vessel into the burette. If this sequence is not observed, the analysis results will be completely wrong.

Combustion. When the gas components have been absorbed, hydrogen and saturated hydrocarbons are burnt. To this end, the cocks *a*, *b*, and *c* are opened to connect the loop containing cupric oxide to the manifold and measuring burette, as well as the cock *2*. The temperature of the loop is raised to 270-300°C with the aid of an electric tube furnace secured on special pins (the temperature must be monitored by a thermometer!). As soon as the prescribed temperature is reached, the gas starts to be slowly transferred from the burette into the vessel with KOH and back (at a rate of 8 to 10 cm³/min). This is done six to ten times with the temperature being carefully monitored and the volume being measured every three or four "pumpings".

As hydrogen is being burnt, it transforms to water and partially reduces CuO in the reaction

$$2H_2 + 2CuO \rightarrow 2H_2O + 2Cu.$$

After the loop has cooled completely (the furnace must be dismantled and removed from the gas analyzer), the residual gas volume is measured. It should be borne in mind that a 3 °C increase in the gas temperature relative to the initial one leads to a 1% error. The gas volume increase corresponds to the volume of burnt hydrogen. The loop is then heated to 850-900°C (the temperature is monitored by a thermocouple). As a result, the methane present in the gas sample reacts with CuO as follows:

$$CH_4 + 4CuO \rightarrow CO_2 + 2H_2O + 4Cu.$$

The residual gas is transferred through the loop at a rate of 10 to 15 cm³/min into the vessel with the KOH solution to a constant volume. The furnace is then removed from the loop, and the latter is cooled. Since at such a high temperature CuO may dissociate releasing oxygen, the latter must be absorbed by the alkaline solution of pyrogallol. Only after this has been done, the residual gas volume is measured. A volume decrement equal to the amount of absorbed CO_2 corresponds to the amount of methane present in the gas.

When unsaturated hydrocarbons are burnt during gas analysis, the gas volume may expand after the combustion. If the loop and its connections with the manifold are completely airtight, this may be the result of presence of other saturated hydrocarbons in addition

to methane in the analyzed gas, primarily ethane C_2H_6. How will this affect the calculations? The presence of both CH_4 and C_2H_6 in the gas makes them difficult.

Let us suppose that by the time the saturated hydrocarbons are burnt, 10.8 cm³ of the gas are left (from a 100-cm³ sample) (see the table below).

Gas volume, cm³	1st combustion	2nd combustion	3rd combustion
After cooling of the loop	16.8	3.25	2.30
After absorption of CO_2 by the alkaline solution	2.9	2.20	2.20
After combustion of CO_2	16.8—2.9 =13.9	3.25—2.20 =1.05	0
After absorption of O_2 released from CuO by pyrogallol	2.85	2.20	2.20

Hence, the total volume of CO_2 after combustion is

$$13.9 + 1.05 = 14.95 \text{ cm}^3$$

The volume of burnt gas is $10.8 - 2.20 = 8.6$ cm³. Denote the ratio $14.95/8.6 = 1.74$ by n.

When only methane and ethane are present in the analyzed gas, the content of one or the other is determined as follows. Denoting the CH_4 volume by v_m and that of C_2H_6 by v_e, we have

$$v_m + v_e = 8.6.$$

The combustion of CH_4 gives v_m of CO_2, while that of C_2H_6 produces $2v_e$ of CO_2 ($C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$). Then, $v_m + 2v_e = 14.95$, hence, $v_m = 8.6 - v_e$. Substitute the value of v_m into the equation: $8.6 - v_e + 2v_e = 14.95$.

Hence, $v_e = 6.35$ and $v_m = 2.25$, that is, if 100 cm³ of the gas have been sampled for analysis, it contained 2.25% of methane and 6.35% of ethane.

The ВТИ-2 gas analyzer (Fig. 129) has found broad application. It consists of six absorption vessels *1* through *6*, a measuring burette *13*, two graduated vertical tubes encased in a protective cylinder *14* with water, a Y-piece with two one-way cocks *15*, a levelling bottle *17*, an expansion loop *12* to neutralize the effect of ambient temperature and pressure fluctuations on the measured gas volumes, devices-ces *11* and *18* for isolating the solutions from the atmosphere, an electric furnace *9* with a ЛАТР-1 autotransformer *10*, a thermometer *8*, a tube or loop *7* for burning the combustible components, a metal strip with clamps and support plates, and a wooden frame *16* serving as a rack supporting all components of the gas analyzer and other auxiliary devices. The operating principle and absorption sequence are similar to the ones described above.

N. S. Torocheshnikov and V. A. Semenova have proposed a chromatographic attachment to the gas analyzer (Fig. 130), which permits cutting down the gas analysis time. In this apparatus, gas is sampled through a cock *19* after the apparatus has been tested for air-tightness
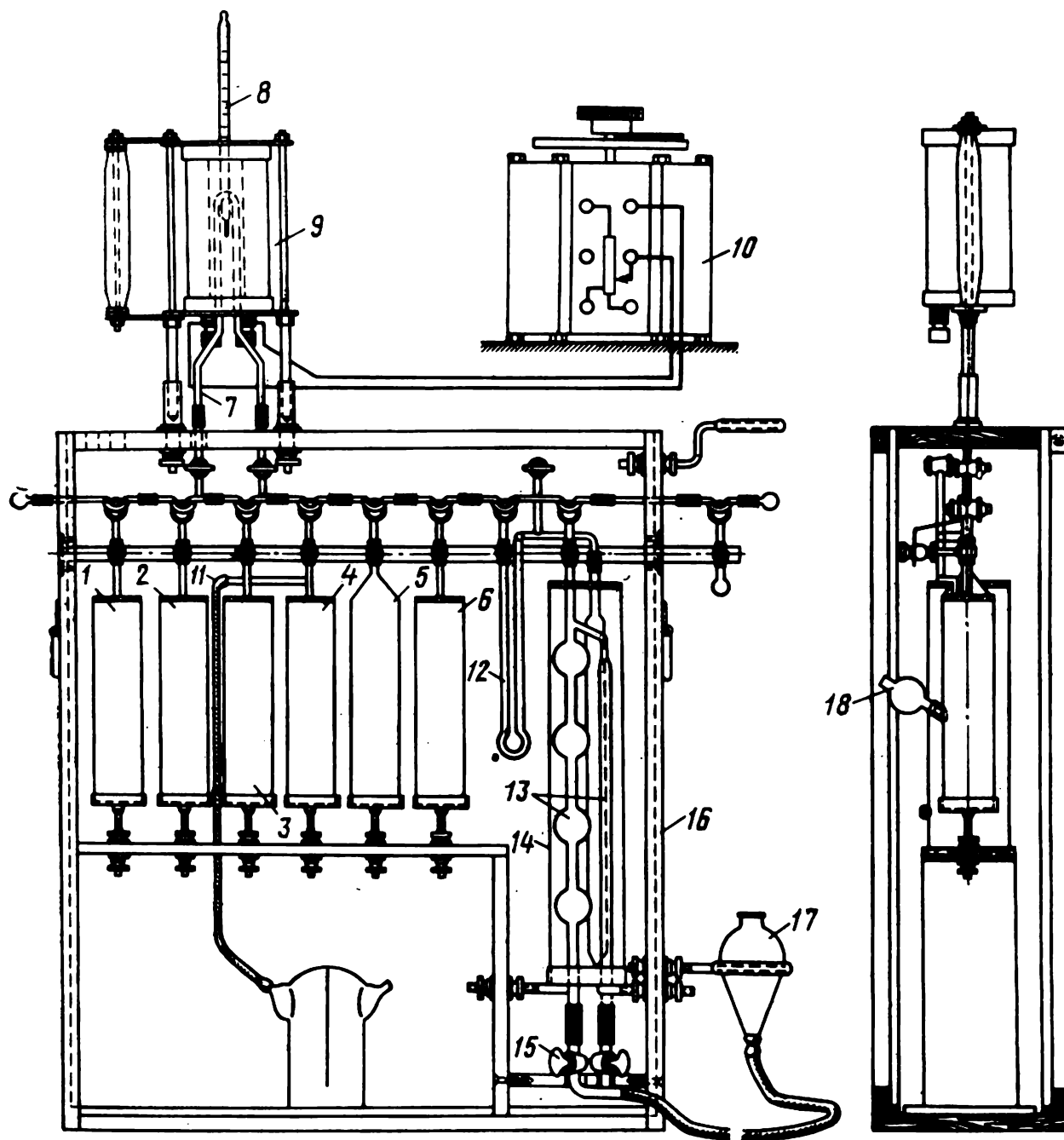
Fig. 129. ВТИ-2 gas analyzer

and all absorption vessels have been filled with respective solutions up to the marks. CO_2, C_nH_{2n}, O_2, and CO are determined in the vessels *16*, *15*, *12*, and *11*, respectively.

The use of the chromatographic attachment is based on the fact that while a gas mixture is being adsorbed in a column with activated charcoal, individual components of the mixture are layered height-wise in the column because of their different adsorptivity, which

is why a CO_2 flow displaces them one after another (sequentially) rather than all at once, and each desorbed mixture component can be determined.

Prior to analysis, the chromatographic attachment must also be tested for air-tightness and filled with carbon dioxide. To do this, CO_2 is passed at a rate exceeding 20 cm^3/min for 2 to 5 min throughout the system then bled into the atmosphere through the cock *1*. Next, the CO_2 feed rate at which the analysis is carried out is set (usually 20 cm^3/min), and the attachment is blown through the cock *4*. The blowing continues with CO_2 being let out through the cock *5*.
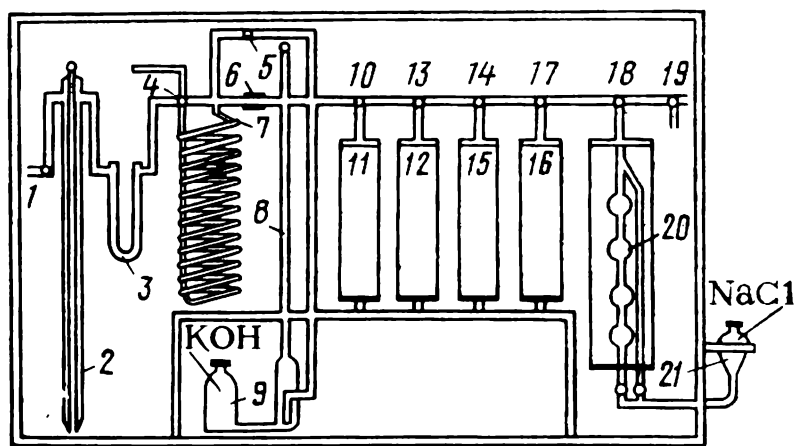
Fig. 130. Gas analyzer with chromatographic attachment

1, 5, 10, 13, 14, 17-19—three-way cocks; *2*—rheometer; *3, 6*—tubes with calcium chloride; *4*—four-way crescent-shaped cock; *7*—chromatographic column; *8*—measuring and absorption burette; *9*—CO_2 bottle; *11, 12, 15, 16*—absorption vessels; *20*—measuring burette; *21*—levelling bottle

To check whether the attachment is filled with CO_2 completely, the cock *5* is periodically turned to establish communication with the measuring and absorption burette *8*. The attachment is considered to be filled with CO_2 if its level in the burette *8* changes according to the presence of other gas traces in CO_2. At a CO_2 feed rate of 20 cm^3/min, the volume must change at a rate not exceeding 0.01 cm^3/min.

After the attachment has been filled with carbon dioxide, the CO_2 supply is cut off (for the sampling period), and its flow is directed into the atmosphere via the cock *1*. In this case, the four-way cock *4* is turned clockwise to the neutral position *E* (Fig. 131). At the same time, the cock *5* is also set to the neutral position (Fig. 130) so that when it is turned to link the adsorption column *7* with the measuring burette *9*, the attachment must not communicate with the atmosphere.

Analytical Procedure. About 20 cm^3 of the gas mixture remaining in the first four absorption vessels are bled into the atmosphere by the cock *4* (position *A*, Fig. 131). At the same time, the gas mix

ture fills the space between the burette and cock *4*. After purging the system, the cock *4* is positioned (by turning it clockwise) so that the next turn would not establish communication with the atmosphere. Then, the liquid level in the right leg of the burette *20* is measured (the left leg is shut off), and the cock *4* is turned to position *B* to supply the necessary amount of the gas (at least 3-4 cm^3) into the adsorption column for chromatographic analysis. The liquid level in the burette *20* is measured with the cock *4* in position *E*. Thus, the difference in the liquid level in the burette *20* before and after the gas is supplied into the adsorption column will correspond to the volume of the sample taken for analysis in the chromatographic attachment (the liquid levels in the burette *20* and levelling bottle *21* must be the same).

The cock *4* is then turned to position *C*, and the CO_2 flowing into the atmosphere is blown through the cock *1* for one minute (after the latter has been turned accordingly). Next, the cock *4* is turned to position *A* for CO_2 to flow into the adsorption column, whereas the cock *5* is positioned for CO_2 to flow into the burette *8* for elution

Fig. 131. Positions of the four-way crescent shaped cock

A—chromatographic column communicates with CO_2 bottle; *B*—burette communicates with column for sampling; *C*—CO_2 vented into the atmosphere; *E*—neutral position before purging the tube with the gas up to the chromatographic column for analysis; *F*—neutral position before feeding the gas to the column

of the gas sample. As soon as gas bubbles appear in the burette *8*, a stopwatch is started, and this instant is registered as the beginning of analysis. In the course of the analysis, the liquid seal level in burette *8* is recorded along with the corresponding time of elution of each component. The components are eluated in the following order: hydrogen, nitrogen, and methane. The analysis is considered to be over after elution of all components present in the gas. At the end of the analysis, the level change in burette *8* must correspond to the blank test, that is the amount of the gas released in the burette per unit time will equal that of traces in CO_2.

It is recommended to take two or three readings of the burette at 10-30 s intervals, at the end of elution of each component. In this case, the liquid level in the burette will practically remain unchanged after the elution.

After analyses, the carbon dioxide flow is cut off, the bottle with CO_2 is shut, and cock *1* is turned to vent the bottle into the atmosphere. This allows avoiding excessive pressures in the chromatographic attachment. The cock *5* is turned to vent burette *8* into the atmosphere to prevent the alkali from being sucked into the chromatographic column. Between analyses, the chromatographic attachment is con-
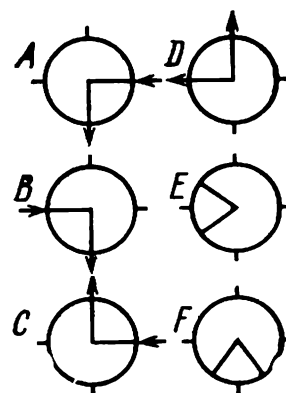
tinuously blown with CO_2 bled into the atmosphere through the cock *5.*

The content of the separated components is calculated from the formula

$$C = \frac{v_f - v_1 - m\,(\tau_f - \tau_1)}{v}\,b = \frac{\Delta v - m\,\Delta \tau}{v}\,b, \qquad (5.56)$$

where C is the content of component in the mixture, in % by volume; v_1 and v_f are the initial and final volumes of the eluated gases, reduced to atmospheric pressure, in cm^3; τ_f and τ_1 are the final and initial component elution times; m is the blank test, in cm^3/min; b is the residual sample after adsorption, in %; and v is the volume of the gas sampled for chromatographic analysis, calculated using the formula

$$v = v_f - v_0 - m\tau_{tot}. \qquad (5.57)$$

where v_0 is the gas volume at the beginning of the analysis, reduced to atmospheric pressure, in cm^3, and τ_{tot} is the time of analysis in the chromatographic attachment, in min.

Gas Density Determination. The density of gaseous products is often determined, in the course of analysis, with the aid of a gas pycnometer (evacuated flask) or by the efflux method. When a pycnometer is used to determine the gas density, it is weighed at first. To this end, it is connected to a vacuum pump with its cock open. After the evacuation, the cock is shut, the pycnometer is disconnected from the pump, and the pump is stopped.

The evacuated pycnometer is weighed on an analytical balance, then filled with the gas of interest. This is done by coupling the pycnometer with a burette and by passing the gas from the burette into the pycnometer until the pressure in both vessels becomes equal to the atmospheric one (the capacity of the burette must exceed that of the pycnometer). After the pycnometer has been filled with the gas, it is disconnected from the burette and weighed again on the same balance.

If G_1 is the weight of the evacuated pycnometer, in g; G_2 is the weight of the pycnometer with the gas, in g; v is the volume of the gas supplied from the burette, in cm^3; t is temperature, in °C; and P is the atmospheric pressure, the gas volume under normal conditions will be

$$v_0 = \frac{vP273}{760\,(273 + t)}. \qquad (5.58)$$

The gas density is

$$\rho = (G_2 - G_1)/v_0\,1000, \qquad (5.59)$$

and with respect to air it will be

$$d = \rho/1.293. \qquad (5.60)$$

To determine the gas density by the effusion method, use is made of the Schilling apparatus (Fig. 132). Its basic component is a glass tube *1* with two constricted portions, placed in a metal protective casing *2*. The tube has its bottom end open and is housed in a glass cylinder with a metal lid *3*. The casing of the tube passes through the lid of the cylinder and has a three-way cock *4* fitted at its top end, through which the glass tube communicates with the atmosphere via a branch pipe *5* or with a metal tube *6* accommodating a platinum plate with an orifice. Water is poured into the cylinder and, with the lid being loose, the glass tube is made to communicate with the atmosphere with the aid of the three-way cock. Connected to the branch pipe is a gas holder with the gas to be analyzed, which fills the glass tube and displaces the water from it. As soon as the gas reaches the lower mark, the glass tube is made to communicate with the atmosphere by the three-way cock through the orifice in the metal tube. The gas will come out through the orifice in the platinum plate. Thus, the glass tube is several times "washed" with the gas.

For determining the gas density, the glass tube is again filled with the gas to a level two or three centimetres below the mark. The three-way cock is turned to let the gas out through the orifice in the metal tube. The moment the water reaches the bottom mark, the stopwatch is started, and the time period during which the water level rises up to the upper mark on the glass tube is measured. The air effusion time is measured in the same manner.

Fig. 132. Apparatus for determining gas density

The gas density with respect to air is calculated using the formula

$$d = \tau_1^2 / \tau_2^2, \qquad (5.61)$$

where τ_1 and τ_2 stand for the gas and air effusion times, respectively.

LITERATURE

Belyanin, B. V. and Erikh, V. N., *Proximate Analysis of Petroleum Products and Gas*, Leningrad, 1975, pp. 7-65.

Tkhorzhevsky, V. P., *Automated Analysis of Gases and Liquids at Chemical Plants*, Moscow, 1976.

Instructions to the Laboratory Work "Gas Analysis"

1. Make sure that all gas analyzer components are clean and all rubber joints and cocks are airtight.

2. Bring up the liquid level in all absorption vessels and the measuring burette up to the marks on the capillaries under the cocks.

3. After the copper in the loop has oxidized to CuO at 400 to 500°C, purge the manifold and loop with nitrogen.

4. During the experiment, make sure that none of the absorbing solutions finds its way into the manifold or the measuring burette. If an absorbing solution penetrates the manifold, disconnect it immediately, wash, and replace the liquid seal with a fresh solution.

5. After the experiment, vent the residual gas into the atmosphere. Bring the level of the absorbing solutions in the vessels and the liquid seal in the burette up to respective marks on the capillaries, and hand the gas analyzer over to the laboratory assistant already prepared for the next analysis.

6. During the gas analysis and determination of unsaturated hydrocarbons, take the necessary precautions when handling bromine water releasing bromine vapours (**work under an exhaust hood!**). (See "Safety Rules to Be Observed in a Chemical Laboratory", section "Toxic Substances".)

LABORATORY WORK 37. CHROMATOGRAPHIC ANALYSIS OF MULTICOMPONENT GAS AND LIQUID MIXTURES

The chromatographic method of separation of mixtures may be defined as a two-phase non-continuous physico-chemical analysis of gas and liquid mixtures, based on repeated extablishment of phase equilibria. In this case, the separated components are distributed between the stationary phase with a large contact area and the mobile phase filtering through the stationary bed.

In gas chromatography, distinction is made between gas adsorption (GAC) and gas-liquid (GLC) partition chromatography.

In GAC, the separation is determined by the adsorptivity of the chromatographic column packing (adsorbent) with respect to the separated gaseous or vaporous compounds. The adsorbents most widely used in GAC include alumina, silica gel, activated charcoal, molecular sieves, and some polymer materials.

In GLC, the separation of the gas mixture components is based on their different distribution between the liquid applied on the surface of a solid inert support and the gas phase. Hence, the separation is based on the difference in the coefficients of distribution, or partition, of components between the mobile and stationary phases. The most common solid supports in GLC are diatomaceous earth, or kieselguhr, firebrick, and pumice. The liquids applied on these supports include esters of high-molecular alcohols, silicone greases, and other substances.

The mobility of the separated components of mixture in gas chromatography is provided by the flow of an inert gas (carrier gas), therefore, the components can be determined both qualitatively and quantitatively at the column exit. The probability that a substance may be present in the gas phase is determined by its distribution in the sorbent-carrier gas system and is expressed in terms of Henry's law constant Ψ for a given substance:

$$\Psi = C_s/C_g, \qquad (5.62)$$

where C_s is the amount of the substance per unit sorbent volume, and C_g is the amount of the substance per unit carrier gas volume.

Thus, if the linear velocity of the carrier gas in the column is w (cm/s), then the speed at which the substance travels through the column takes the form

$$w_{eff} = w/\Psi. \qquad (5.63)$$

If the sample is a mixture of several substances with the Henry constants of these substances being different for the sorbent involved, the substances will travel through the column at different speeds, which will result in their complete separation if the column is sufficiently long. If the difference between the Henry constants of the mixture components is small, the separation can be achieved by lengthening the column (however, its resistance will increase) or by using a more selective sorbent.

The major advantages of gas-liquid chromatography over the gas-absorption one are the possibility of wide selection of stationary liquids having various chemical structures and molecular weights, as well as their homogeneity. Owing to this, the isotherms of solubility are practically linear within a broad range of concentrations. Commercial adsorbents, however, are chemically and structurally inhomogeneous to a large extent.

Among the serious disadvantages of gas-liquid chromatography are the volatility and instability of liquid phases, which makes it impossible to analyze by this method over a long period of time and at elevated temperatures.

Owing to the high mass transfer rate, GAC is highly effective in rapid analyses, particularly if non-porous or porous-surface adsorbents are used.

The basic components of a chromatographic system are as follows (Fig. 133): (a) source of the carrier gas (usually a gas bottle) with a device for controlling pressure and the gas flow rate (pressure regulator, fine adjustment valve); (b) chromatographic column packed with an adsorbent of a liquid phase support, which may be made as a straight, U-shaped or coiled tube of various materials (stainless steel, glass, polymer); (c) sample injector for introducing the mixture to be analyzed into the column; (d) detector for monitoring the variations in the composition of the substances coming out of the column; (e) recorder for automatic recording of the analysis results; and (f) thermostat for controlling the temperature of the vaporizer, injected samples, column, and detector.

All chromatographic system components are arranged in respective units of laboratory chromatographs. The carrier gases are usually hydrogen, helium, nitrogen, argon, and air. The carrier gas must be inert, ensure high sensitivity, be readily available, safe, pure, and

relatively cheap; its viscosity must be as low as possible to avoid high pressure gradients in the column, whereas the diffusion characteristics must be optimal for the limiting step of the process.
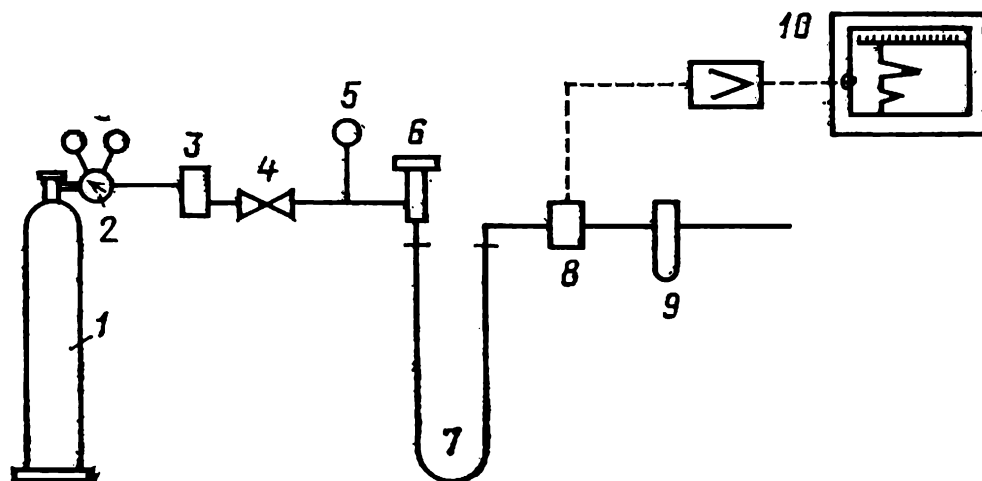
Fig. 133. Chromatographic system

1—carrier gas bottle; *2*—pressure regulator; *3*—desiccator; *4*—carrier gas flow control valve; *5*—pressure gauge; *6*—sample injection unit; *7*—column; *8*—detector; *9*—flow meter; *10*—detector circuitary and recorder

The appearance and quality of the chromatogram which determines the analysis results depend on the sample volume and the way in which it is injected into the chromatograph. The highest efficiency is attained when the sample occupies a volume corresponding to a theoretical plate and when this volume is injected instantaneously and in a plug flow.

Chromatographic columns are normally 1 to 4 m long. The temperature maintained in the column thermostats must be sufficiently high to cut down the analysis time and sufficiently low to ensure the required separation. A column must be filled uniformly and densely by means of a water-jet pump (Fig. 134). The uniformity of the gas-air mixture flow is determined by the sorbent grain shape and size range.

Fig. 134. Filling of the column

1—adsorbent; *2*—funnel; *3*—chromatographic column; *4*—fibre wad; *5*—Drexel bottle

The ultimate purpose of chromatographic analysis is to derive an elution curve (Fig. 135) which is given, for an individual component, by the equation

$$C_{ex} = C_0 f(\Psi, v), \qquad (5.64)$$

in which C_{ex} is the component concentration in the carrier gas at the column exit, C_0 is the component concentration in the carrier gas at the column inlet at the moment of sample injection, and v is the volume of the carrier gas passed through the column
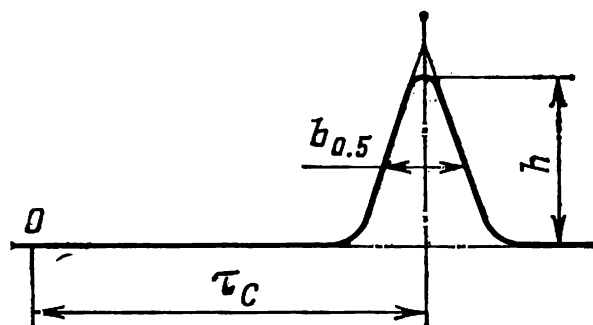
Fig. 135. Chromatographic peak parameters

O—sample injection; $b_{0.5}$—peak half-width; τ_c—component retention time; *h*—peak height

Since the carrier gas flow rate is maintained constant, the retained volume v_c of the separated component is calculated from the formula

$$v_c = V\tau_c, \qquad (5.65)$$

where V is the flow rate of the carrier gas, reduced to normal conditions, in cm^3/min, and τ_c is the separated component retention time.

In gas-adsorption chromatography,

$$v_c = SL\ \Psi_{true}, \qquad (5..66)$$

where Ψ_{true} is the Henry adsorption constant per unit volume of the porous material, in cm^3/cm^3; S is the column cross-sectional area, in m^2; and L is the column length, in m.

In gas-liquid chromatography,

$$v_c = m/\rho K_p, \qquad (5.67)$$

where K_p is the partition coefficient per unit volume of the liquid phase, in cm^3/cm^3; m is the mass of the liquid phase introduced into the column, in kg; and ρ is the density of the liquid phase in the column, in kg/m^3.

Most commonly used in practice is the relative retention volume

$$v_{rel} = v_c/v_{ref}, \qquad (5.68)$$

where v_{ref} is the retention volume of the substance used as a reference.

The detector has a different sensitivity to each sample component, which is why the areas and heights of the component peaks will not be directly proportional to the component contents. Then, it is necessary to define the correction factors which will be different for

different compounds. The correction factors for most components are listed in reference books or can be calculated from the formula

$$K_i = g_i S_{ref}/g_{ref} S_i, \qquad (5.69)$$

in which g_i and g_{ref} stand for the weights of the sample and reference, respectively, S_{ref} and S_i are the peak areas of the reference and sample, respectively. The area of a chromatographic peak is determined as the product of its height by half its width (Fig. 135):

$$S = h b_{0.5}.$$

This work includes several assignments involving chromatographic analysis of the starting components and end products.

A. EFFECT OF THE SAMPLE INJECTION TECHNIQUE ON THE ACCURACY OF ANALYSIS RESULTS

This assignment shows how to inject a sample by a syringe and a sample inlet valve and the associated reproducibility.

The experimental conditions are as follows: chromatograph ЛХМ-8МД (model 1 or 2); carrier gas—nitrogen; carrier gas flow rate—40 cm³/min; thermostat temperature—70°C; thermal conductivity cell current—100 mA; column length—1 m; column internal diameter—3 mm; sample volume—1.0 cm³; adsorbent—charcoal of any commercial grade, having a particle size of 0.25 to 0.5 mm; adsorbate—1.25% mixture of natural gas with air.

Before the experiment, the chromatograph is made to operate under the specified conditions, and ten similar samples are injected from a gas burette by means of the sample inlet valve at 1 min intervals. The chromatogram scale is selected so that the height of the methane peak falls between 50 and 90% of the recorder scale. Then, 1 cm³ of the analyzed mixture is injected by a microsyringe into the corresponding channel of the vaporizer (ten similar samples are injected in this manner one after another at 1 min intervals). The methane peak height is measured in millimetres, and the average height is calculated along with the error of an individual determination and the relative mean error for each sample injection technique.

The sample injections by the valve and by the syringe are compared on the basis of the relative mean error. If it exceeds 3%, the experiment must be repeated. The results are tabulated as follows:

Experiment number	Peak height		Error of individual determination		Mean error		Relative mean error	
	valve	syringe	valve	syringe	valve	syringe	valve	syringe

Example of Calculation. The methane peak heights resulting from injection by the valve or syringe (mm) are: $h_1 + h_2 + h_3 = h$; $130 + 134 + 133 = 397$. The average peak height is $397 : 3 = 132.3$ mm. The error of an individual determination (mm) is: $130.0 - 132.3 = -2.3$; $134.0 - 132.3 = 1.7$; $133.0 - 132.3 = 0.7$. The mean error (mm) is: $4.7 : 3 \cong 1.6$. The relative mean error is: $(1.6 \cdot 100 : 132.3) = 1.2$.

B. SEPARATION OF METHANE-AIR MIXTURE*

This assignment involves separation of a methane-air mixture and calculation of the chromatogram.

The analysis conditions are as follows: column length—1.5 m; column internal diameter—6 mm; adsorbent—molecular sieves (zeolites CaX or NaX, 5 Å); carrier gas—helium (hydrogen); carrier gas flow rate—100 cm³/min; temperature—20°C (room).

Before the experiment, the chromatograph is made to operate under the specified conditions. The recorder is switched on and its pen is set by the coarse and fine zero setting knobs at a distance of 1 cm to the right of the beginning of the scale. If the chromatograph operates under steady-state conditions, the recorder draws a straight line. The chromatogram of the methane-air mixture is taken, and the retention volumes of nitrogen and methane relative to oxygen are calculated using the formula

$$v_{rel} = l/l_{ref}, \qquad (5.70)$$

where l and l_{ref} stand for the distances, on the chart strip, between the sample injection moment and the peak maxima of the sample and reference (l varies directly with τ_C).

The components resulting from separation of the methane-air mixture come out in the following sequence: oxygen, nitrogen, and methane. The results are tabulated as follows:

Substance	l, mm	v_{rel}
Oxygen Nitrogen Methane		

C. QUALITATIVE AND QUANTITATIVE ANALYSIS OF MIXTURE OF AROMATIC HYDROCARBONS**

In this assignment it is necessary to calculate the retention volumes of individual hydrocarbons relative to cyclohexane.

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* The assignment forms part of Work 18.
** The assignment forms part of Work 9.

The analysis conditions are as follows: column length—1.5 m; column internal diameter—6 mm; stationary phase—polyethylene glycol adipate or dinonyl phthalate taken in an amount of 10% by weight of the solid support (firebrick of the ИНЗ-600 grade, particle size—0.25 to 0.5 mm); carrier gas—helium (hydrogen); carrier gas flow rate—100 cm³/min; column temperature—80°C.

The sequence in which the experiment is carried out is similar to the previous assignment.

The results of chromatographic analysis of the components separated during pyrolysis of petroleum products are tabulated as follows:

Substance	l, mm	v_{rel}
Cyclohexane Benzene Toluene Ethyl benzene		

Peak number	l, mm	v_{rel}	Substance	$b_{0.5}$, mm	h, mm	S, mm²	$K \cdot S$	Substance content, %, by weight

The relative retention volumes of the mixture components are compared with those of hydrocarbons, and the components are identified.

The chromatograph is calibrated. The calibration factor for benzene is taken equal to unity. The results are tabulated as follows:

Mixture	Sample, weight, g	h	$b_{0.5}$	S	K_i
Benzene Toluene Benzene Ethyl benzene					

The composition of the analyzed mixture is calculated from the formula

$$C_i = \frac{K_1 S_1}{\sum\limits_{i=1}^{n} K_1 S_1} \, 100. \tag{5.71}$$

D. ANALYSIS OF A MIXTURE OF ALKYL
AND ALKYLENE BENZENES*

This assignment involves separation and calculation of the composition of a mixture of ethyl benzene and ethylene benzene.

The analysis conditions are as follows: column length—2 m; column internal diameter—3 mm; column thermostat temperature—100°C; vaporizer temperature — 200°C; carrier gas—helium; carrier gas flow rate—40 ml/min; detector current—130 mA; stationary phase—15% by weight of 1, 2, 3, 4-tetracyanoethoxymethylmethane (Tetrakis) on Chromaton N (particle size—0.16 to 0.25 mm); sample volume—1 to 2 cm³; component emergence time—ca. 12 min.

The experimental procedure is the same as in Assignment B. The sample is injected into the chromatograph via the vaporizer by a microsyringe. The content of an individual mixture component is determined from the ratio between the area of the peak corresponding to this component and the sum of all peak areas. In the separation of this mixture, the correction factors are assumed to equal unity. The results are tabulated as follows:

Substance	Sample volume, cm^3	Peak height h, m	Peak half-width $b_{0.5}$, 0.5 m	Peak area S, m^2	Correction factor K

E. SEPARATION AND QUANTITATIVE ANALYSIS
OF MIXTURES CONTAINING O_2, N_2, CO, CH_4, AND CO_2**

This assignment calls for separation of a mixture containing O_2, N_2, CO, CH_4, and CO_2 as well as calculation of its percentage composition using molar correction factors (Table 21).

Table 21

Compound	Hydrogen, reference n-butane	Helium	
		Reference n-butane	Reference benzene
Nitrogen	1.76	2.02	2.38
Oxygen	1.95	2.12	2.50
Carbon monoxide	1.87	1.77	2.38
Carbon dioxide	1.55	2.02	2.08
Methane	2.03	2.36	—

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* The assignment forms part of Work 16.
** The assignment forms part of Work 14.

The chromatographic system comprises two glass columns, a detector, rheometers for measuring the carrier gas flow rates at the inlet and outlet of the columns, and a valve for injecting the gas sample into the columns of the chromatograph.

The analysis conditions are as follows: carrier gas—hydrogen; outlet carrier gas flow rate—30 cm^3/min; column and transducer temperature—20°C. The first column (GLC) is 2 m long and 4 mm in internal diameter. The stationary phase is triethylene glycol di-(2-ethyl butyrate) taken in an amount of 25% by weight of the solid support which is inert firebrick of the ИНЗ-600 grade having a particle size of 0.25 to 0.5 mm and precalcined at 1000°C. The column is intended to separate air, CO_2, and gaseous hydrocarbons. The compounds O_2, N_2, CO, and CH_4 are not separated on the above packing.

The second column (GAC) is 1.5 m long and 4 mm in internal diameter. The adsorbent is in the form of molecular sieves CaX having a particle size of 0.25 to 0.5 mm and activated at 600°C for 4 hours. This column serves to separate O_2, N_2, CO, and CH_4.

Both columns are connected in series through a glass coil 2 m long and 4 mm in internal diameter, intended to slow down the gas flow. The gas sample is injected by the valve into the first column. The components emerging from this column are detected by the reference cell of the detector. As it emerges from the reference cell, the gas sample passes through the coil and enters the second column. The components separated in the second column are detected by the measuring cell of the detector.

The chromatograms are calculated in the same manner as in the previous assignments.

LITERATURE

Vorozhbitova, L. N. and Plachenov, T. G., *Application of Gas Adsorption Chromatography in Studying the Sorption Properties of Adsorbents*, Leningrad, 1976.

Golbert, G. A. and Vigdergauz, M. S., *A Course in Gas Chromatography*, Moscow, 1974.

Instructions to the Laboratory Work "Chromatographic Analysis of Multicomponent Gas and Liquid Mixtures"

1. Before the experiment, test the system for air-tightness.

2. When using a gas bottle, make sure that it is always capped while not in use. The bottle must be protected against heating.

3. When using a gas bottle, first open the pressure regulator, then carefully turn the discharge valve so that the gas flows out at a particular pressure.

4. Make the chromatograph to operate under the specified conditions under the instructor's supervision. Use the manual supplied by the manufacturer with the model used.

5. Avoid contact between the Dewar flasks and oils or greases (**explosion hazard!**).

6. When immersing the adsorbent with the sample into liquid nitrogen, avoid contact between the adsorber and the Dewar flask to prevent breakage of both the adsorber and the Dewar flask.

Appendix

Safety Rules to be Observed in a Chemical Laboratory

Permission to work in a chemical laboratory is given to persons who have been instructed in safe experimental procedures, know how to handle chemical reagents, reaction products, and synthesized compounds, are familiar with their toxicity as well as the fire and explosion hazards involved, and can render first aid in the case of poisoning, burns, electrocution, and other accidents.

Even the slightest carelessness and negligence in a chemical laboratory may lead to accidents with grave consequences. Most accidents occur as a result of careless work, non-observance of the safety rules and approved procedures, or insufficient knowledge of the properties of the chemicals used in experiments. No experiment should be started before all reaction steps, their conducting and monitoring procedures are made absolutely clear. Particular care must be taken in handling toxic, explosive, caustic and highly inflammable substances.

Work in a chemical laboratory will be safe if all those concerned carefully think over every procedure, constantly observe the safety rules, and are fully aware of the dangers involved.

I. General Rules

1. Be as careful as you possibly can in carying out every procedure, bearing in mind that sloppiness, inattentiveness, and insufficient knowledge of the instruments, apparatus, and properties of the substances used in experiments may lead to accidents.

2. In carrying out a laboratory work, perform only the given and explained assignment without being distracted by irrelevant matters.

3. Conduct chemical reactions only using amounts and concentrations of substances, laboratory ware and apparatus, and experimental procedures specified in appropriate manuals and prescriptions.

Any experiment may only be conducted after a preliminary test run on a smaller scale and taking all the necessary precautions. Everyone involved in an experiment must plan it from the standpoint of safety. The first experiments with new substances must be carried out only under the instructor's supervision using all the necessary protective devices.

4. In experiments involving the use or synthesis of substances with little known properties, take into account the posibility of formation of products with dangerous properties that cannot always be predicted. Therefore, carry out such experiments under properly operating exhaust hood with its door closed, wearing, if necessary, a protective mask and rubber gloves, as well as erecting protective walls around the experimental setup.

5. Do not eat, drink, or smoke at the working station. Carefully wash your hands after work.

6. Never taste chemicals in the laboratory. Smell chemicals with extreme care. Do not inhale deeply but drive the vapours or fumes toward your nose by a sweeping motion of the hand. Before you smell a chemical, make sure it is not toxic.

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7. Handle all unknown chemicals as if they were toxic, as practically all chemicals are more or less noxious. Hence, a good rule of thumb—before pouring a chemical into a flask (bottle), paste on it a label with the name and concentration (density) of the chemical.

8. Carry out all experiments with noxious gases or substances releasing noxious vapours or gases (cyan compounds, chlorine, bromine, hydrogen sulphide, ammonia, organic solvents, volatile acids, etc.) only under a properly working exhaust hood with its door closed. In the case of failure of the ventilating system motor, stop the experiment immediately.

9. Handle caustic and noxious substances wearing a buttoned down smock, making sure that these substances do not come in contact with your skin or clothes.

10. To preclude vigorous boiling and splashing of a liquid heated to boiling, place a few capillaries having their top ends sealed in the vessel, or pieces of porous porcelain. The latter can only be put into a cold liquid. Never throw them into a liquid heated to boiling.

During the experiment and, particularly, heating, do not lean over the vessel in which a reaction is being conducted. When a reaction is being conducted in test tubes, do not point their open ends at yourself or at the people standing nearby.

11. In experiments with caustic, toxic or explosive substances, carried out at low or high pressures, and whenever carelessness, disturbances in the course of the process, or any other factors may cause damage, burning, irritation, or contamination of your eyes, wear protective masks, goggles, acrylic plastic shields, wire nets, and the like.

12. In carrying out an experiment in which a gas is released in the apparatus or a liquid is heated, be careful to avoid an increase in pressure and an explosion as a result of clogging of the discharge pipe, too high resistance in the washing or absorption bottles, and so on.

13. Carefully check the setup and laboratory ware before every procedure, making sure that they are in proper condition and correctly assembled. Do not send the laboratory ware to be washed together with other vessels without having first neutralized the toxic substances.

14. Do not leave any substances in vessels having no labels or inscriptions. When taking a reagent, read the label, and if you have the slightest doubt, inquire about it or check.

15. Do not pour or throw the remnants of inflammable, explosive, toxic and malodorous substances into sinks or garbage cans. Collect them in specially provided vessels and dispose of them, after they have been properly treated, into an appropriate well. Only water and neutral solutions may be poured into sinks.

16. Keep the laboratory clean. Make sure that the working station is free of anything that has nothing to do with the experiment. Do not encumber tables with laboratory ware, equipment, reagents, and the like (not necessary at the moment), particularly with vessels containing concentrated acids and alkalis, explosive and inflammable substances.

17. Keep the accesses to the fire-fighting equipment (boxes with sand), sinks, switchboards, and the like free. Do not block them even for a short period of time.

18. Do not work alone in the laboratory; at least two people must be present, one of them responsible for the experiment.

19. When leaving the laboratory, make sure that all heating devices are switched off and the gas valves and water taps are closed.

20. When carrying out an experiment, take all the necessary precautions for the event of cutoff of the water, electric power, gas, or ventilating air supply. When the water or gas supply is cut off, close all the valves, cocks, and taps. In the case of power failure, switch off all electric appliances.

II. Rules for Safe Handling of Caustic Substances

1. Caustic substances include acids (hydrochloric, nitric sulphuric, hydrofluoric, and chromic), solid alkalis (sodium and potassium hydroxides), their concentrated solutions, ammoniacal brine, bromine and its solutions. When caustic substances contact the skin, they cause burns similar to thermal ones. They are particularly dangerous for the eyes.

2. To avoid burns in handling caustic substances under any conditions, wear protective goggles (or acrylic plastic shields), rubber gloves and, in some cases, rubberized aprons and rubber boots (when mixing and carrying acids and alkalis). Handling acids and alkalis without protective grab is forbidden.

3. Keep acid and alkali bottles in intact baskets or latticework, carry them only together with another person, and transport them on a specially designed cart.

4. Decant acids and alkalis from large bottles into smaller vessels using siphons with rubber bulbs or hand pumps. Decant ammoniacal liquor, bromine, and volatile concentrated acids only under an exhaust hood. Always wear goggles, gloves, an apron, and a B gas mask.

5. In preparing sulphuric acid solutions, pour it into water in a narrow stream with incessant stirring to avoid local heating and splashing of the acid on those standing nearby. Do not pour water into sulphuric acid.

6. Collect and neutralize spent acids and alkalis separately.

7. Dissolve alkalis by slowly adding small pieces of an alkali to water with continuous stirring. Crush large lumps of an alkali into small pieces under a cloth (belting).

8. Hydrofluoric acid inflicts slowly healing wounds and causes inflammation of the lungs. When it contacts the skin, wash the latter with a strong jet of water and put on a compress with 5% solution of soda.

9. When washing laboratory ware with a chromic acid mixture, avoid its contact with your skin, shoes, and clothes.

III. Rules for Safe Handling of Highly Toxic Substances

When handling highly toxic substances (hydrocyanic acid and cyanides, mercaptophos, carbon disulphide, arsenic oxides, etc.), be especially careful and strictly follow "The Instructions for Authorization to Produce, Sell, Buy, Store, and Transport Highly Toxic Substances and Poisons by Civilian Organizations".

IV. Safety Rules to Be Observed in Experiments Involving Explosion and Fire Hazards

1. When carrying out experiments involving an explosion hazard, always wear protective masks, work behind shields and screens, provide for the necessary enclosures, or place the apparatus in special chambers.

2. Do not heat or simply mix inflammable substances with strong oxidizing agents to avoid spontaneous combustion or explosion.

3. Prepare the ammonia solution of silver oxide before each experiment in an amount required for the experiment, because in storage it forms fulminating silver.

4. The chemical ware used in experiments under a high pressure or vacuum must be tested in advance for strength. Use only round-bottomed flasks and, at normal temperatures, thick-walled ware. Place glass vessels in protective hoods (net, cloth).

5. When working with oil or paraffin wax baths, protect them against contact with water. When heated under a layer of oil, small amounts of water become overheated and cause the hot oil to splash out.

6. Vessels in which highly inflammable liquids were kept contain explosive mixtures which is why they must always be washed with water.

7. Always remember that dimethyl, diethyl and other ethers form peroxides in storage, which may cause severe explosions normally occurring at the end of distillation of an ether. Therefore, before using ethers, check whether they contain peroxides. If so, remove the peroxides. Heat ethers only on a hot bath after the source of heat has been moved away to a distance of at least 5 m.

8. Remember that some inflammable vapours and gases ignite even in the absence of an open flame or spark, depending on temperature and pressure (see Table 2).

Rags, towels, and overalls stained with oil and oxidizers are especially prone to spontaneous combustion.

V. Rules for Safe Handling of Inflammable and Explosive Substances

1. When handling combustible substances and, particularly, highly inflammable liquids, do not heat them on an uncovered fire or on a grill and do not keep them near an open flame. Heat such substances and distill them on a water, oil or air bath with electric heating by heaters with concealed heating elements and electric wires.

2. Handle highly inflammable and combustible substances (toluene, xylene, chloroform, dimethyl and diethyl ethers, alcohols, esters of organic acids, etc.) only under an exhaust hood in the absence of an open flame.

3. When heating highly inflammable liquids taken in an amount exceeding 0.5 l, place a tray of a sufficient capacity underneath for the liquid to drip into it in the case of an accident. Wash the vessels immediately after work.

4. If an inflammable liquid has been spilled by accident, immediately switch off all heating devices and burners, and pour sand on the puddle to be at once swept away by wooden shovels. In case of fire, call the firemen and try to put out the fire by fire extinguishers, sand, and an asbestos blanket. Do not use water to extinguish burning liquids immiscible with water.

5. Almost all combustible liquids are volatile and are harmful for the human organism, so handle them only under an exhaust hood.

The absence of ventilation and use of short coolers may lead to formation of explosive mixtures in air, which may eventually explode.

6. Do not store combustible substances near flames and heating devices. such as thermostats, electric furnaces, radiators, etc. Keep combustible substances at your working station in an amount necessary for the work under way. Combustible liquids may be stored in the laboratory (in an amount not exceeding the daily requirement) in thick-walled vessels put in closed metal boxes. The latter must be located far from exits so as not to block aisles. Keep ether in a corked bottle with a glass tube stretched into a capillary or a calcium chloride tube passing through the cork. The walls and bottom of the box must be lined with an asbestos sheet. The inner side of the box lid must bear a list of what is stored inside, indicating the amount allowed for storage.

7. Never store low-boiling substances (divinyl, isoprene, diethyl ether, acetone, etc.) in the laboratory. After work, take these substances out of the laboratory for storage in a separate room (warehouse).

8. Store diethyl (ethyl) ether isolated from other substances in a cold and dark room, because its exposure to light leads to the formation of an explosive substance—ethyl peroxide.

9. Carry combustible substances from the store to the laboratory in a glass vessel put in an iron container filled with sand.

10. Store organometallic compounds in sealed ampoules which must be buried in sand to at least half their height, and close the box with the sand tightly. Carry the box carefully without shaking it.

11. Decant small amounts of combustible liquids only far from a flame. When decanting large amounts of highly volatile liquids, put out all burners and heaters in the room.

12. When handling inflammable liquids, always remember that a flask may crack or burst during work, therefore, take the necessary measures to protect the experimenter from splashing of the burning liquid (e.g., put a fire-proof screen).

13. When working with oil baths, always insert a thermometer into the bath and make sure that the oil is not heated to a temperature above the ignition point.

14. Do not pour combustible liquids into the plumbing system. Collect the spent liquids in a special tightly closed vessel which must be removed from the laboratory at the end of the work.

VI. Rules for Safe Handling of Combustible Gases and Vapours

1. Do not ignite hydrogen and other combustible gases or vapours without having tested them for purity in a test tube.

2. When assembling apparatus for experimentation with combustible gases and vapours, use flame traps—protective tubes with copper meshes (use an iron mesh for acetylene). Do not use sand baths for heating test tubes.

3. Before adding a gas to a gas holder, test the gas already in the gas holder by taking a sample in a test tube.

4. Keep gases in a gas holder under the pressure of water in a funnel.

5. To avoid formation of an explosive mixture, replace the water when filling a gas holder with fresh gas (see Table 3).

Before passing a gas through vessels previously containing some gases, purge the latter by blowing or sucking air through them.

VII. Rules for Safe Handling of Liquid Oxygen, Nitrogen and Air

1. In contact with organic substances, oils, and greases, liquid air and oxygen form explosive mixtures, therefore, protect vessels with liquefied air or oxygen to keep away organic substances. Carry out all experiments wearing clean garb, protective goggles, and gloves, and make sure that no contaminants find their way into the vessels.

When liquid air, oxygen and nitrogen contact the skin, they cause frost-bites, therefore, protect your skin and especially eyes against contact with liquid gases.

2. Place glass Dewar flasks and other glass and quartz vessels with double walls, intended for liquid gases and coolants, in a protective casing, making sure that they are clean and dry. Do not handle such vessels without protective casings.

3. Pour liquid gases (air, oxygen, nitrogen) into Dewar flasks only through a metal funnel not touching the flask walls. The funnel tube must be longer than the flask neck.

4. Cool organic liquids by liquid air with the aid of a copper coil immersed into the organic liquid. Pass liquid air through the coil. Do not use liquid nitrogen for cooling traps and other vessels intended for condensation of low-boiling organic substances because the oxygen present in air may condense in the cooled vessels.

5. Do not use pure liquid oxygen undiluted with nitrogen for cooling purposes.

The use of pure oxygen is allowed only in preparing a mixture with liquid nitrogen to increase its boiling point (1 : 3).

6. Do not keep more than one Dewar flask with liquid gases in the laboratory. The vessels with liquid gases must always be capped. The vessel with liquid oxygen must bear the inscription "oxygen".

Keep the laboratory in which experiments with liquid oxygen are carried out cleaner than usual.

7. Handle liquid oxygen wearing clean garb. Wash your hands with soap.

Do not contaminate liquid gas containing vessels with oil and other organic substances.

Do not keep oily waste, rags, and other combustible materials at the working station.

VIII. Rules for Safe Handling of Mercury

1. Metallic mercury is widely used in laboratories, both exposed and in instruments. **The vapours of mercury and most of its compounds (salts) exhibit high cumulative toxicity. The maximum permissible concentration of mercury vapours in the surrounding air is 0.01 mg/m³.**

2. Mercury vapours are absorbed by plaster, wood, fabrics, rust, and other substances, thereby creating sources of intoxication during subsequent desorption. When metallic mercury is dropped on the floor, it forms tiny droplets capable of penetrating into pores and cracks in the walls, floors, and furniture, from which it then evaporates. Specially prepared rooms meeting the requirements of the instructions written for the purpose are provided for handling mercury.

Instruments in which mercury is encapsulated (pressure gauges) are allowed to be installed in the laboratory on enameled or painted trays with high edges.

3. Store mercury in stoppered and capped bottles, each containing not more than 1 kg of mercury. Keep the bottle with mercury in a rubber bag or in a metal can under an exhaust hood. Do not store mercury in flasks made of thin glass or under water in open vessels.

4. Do not keep unused or broken mercury-containing instruments in the laboratory.

5. Immediately collect accidentally spilled mercury with the aid of a glass trap (two-necked bottle) with a rubber bulb or a pump. To collect the tiniest mercury droplets, use amalgamated copper plates. Then, treat the floor with a 3% solution of potassium permanganate with addition of 5 ml of concentrated hydrochloric acid per litre of the solution or a 20% solution of ferric chloride. After demercurization, analyze the ambient air for presence of mercury. Continue work in the laboratory after the air analysis results prove to be negative.

6. Analyze the air in rooms where exposed mercury is handled periodically, at least four times a year. When the air is found to contain mercury vapours in a concentration above the permissible level, all work has to be stopped, the room must be demercurized, and the air analyzed.

7. Handle mercury wearing a buttoned down smock and a cap (or a kerchief); in handling toxic mercury salts, also wear rubber gloves. After work and before meals, wash your hands and face with warm water and soap, and rinse your mouth with a diluted solution of potassium permanganate. For individual protection in the case of high mercury vapour concentrations, use a commercial gas mask of the Γ type (iodine-impregnated activated charcoal).

8. Do not use cleaning utensils designed for rooms in which mercury is handled to clean other rooms, and keep them in the bottom compartments of the exhaust hood. Paint these appliances red for identification.

9. Those who handle mercury must undergo a medical examination at least once a year.

IX. Rules for Safe Handling of Chemical Glassware

1. To avoid injuries while cutting glass tubes, assembling and disassembling glass apparatus and components, observe the following safety rules:
(a) break glass tubes only after notching them with a file or a special glass cutter, with your hands wrapped in a towel;
(b) melt the sharp edges of tubes on a gas flame and cool them on asbestos.
2. When stoppering a thick-walled vessel, hold it by the upper part of the neck, closer to the stopper, with your hands wrapped in a towel for protection.
3. Do not plug a heated vessel with a ground-glass stopper before it is cooled.
4. In mixing liquids, use a funnel mounted into a porcelain triangle or the rack ring above the receiver of the liquid.
5. Use a towel when carrying a vessel with a hot liquid, holding the vessel by its bottom and neck.
6. Carry out all work, which might result in an increase in pressure inside the vessel, overheating, and breakage with splashing of hot liquids, under an exhaust hood using protective plastic shields.
7. When mixing and dilution of substances involves heat release, use refractory glass or porcelain vessels.
8. Wrap all evacuated vessels in a metal gauze, and use a trap during vacuum distillation with a water-jet pump to prevent noxious chemicals from flowing into the plumbing system.
9. Before sealing glass vessels in which highly inflammable liquids or combustible gases were contained, empty them completely and purge with nitrogen.
10. Encapsulate in glass ampoules only condensed gaseous substances boiling at a temperature of not less than 20°C. Do not encapsulate substances which decompose when heated and explode.
11. Seal, open and store ampoules in compliance with instructions for handling sealed ampoules.

X. Rules for Safe Operation of Electrical Equipment and Appliances

1. Electric current may cause fire, explosion, and electrocution. The causes of accidents may be:
(a) short circuits, consumption of current of an intensity greater than the wire cross-section can withstand, plugging wires into faulty sockets, etc.;
(b) explosive mixtures of gases in the laboratory, transformer oil near a burning wire, a faulty gas pipe;
(c) touching bare wires or unearthed equipment with hands or metal objects (electrocution);
(d) careless use of electric appliances.
2. When finding a defect in the insulation of wires, knife switches, sockets, plugs, and other accessories, in earthing, or in safeguards, immediately report to the electrician on duty.
3. All faults in electric appliances, wiring accessories, electric network, and other equipment are to be removed only by the electrician.
4. All high-voltage installations must bear signs with a red zigzag arrow and the inscription "Do not touch. High voltage—danger!".
5. Portable lamps must be rated at not more than 36 V (12 V for damp environments).
6. Do not: (a) use improvised fuse links instead of plug fuses; (b) work near bare wires; (c) block passages to switchboards; (d) open switchboards; (e) hang different objects on electric wires and appliances.

7. If the power supply is cut off or a phase fails, switch off all electric appliances and motors immediately.

8. If wires or electric appliances catch fire, de-energize them at once and put out the fire by a dry CO_2 fire extinguisher and an asbestos blanket.

9. When somebody is electrocuted, cut out the knife switch on the switchboard to de-energize the wires responsible for the electrocution.

XI. Rules for Safe Handling of Bottles with Compressed and Liquefied Gases

1. All gas bottles must have a protective cap, and those containing toxic gases must additionally be provided with a plug on the side nipple. Bottles containing hydrogen and other combustible gases have a left-hand thread on the nipple, while those containing oxygen and other noncombustible gases have a right-hand thread to avoid mistakes in filling the bottles. All bottles are identified by the paint colour, marking (band), and name of the contained gas. Check whether a gas bottle bears a test stamp (e.g. stamped numerals 5-65-70 indicate that the bottle was tested in May, 1965, followed by another test in 1970). Do not use gas bottles whose testing is overdue.

2. Bottles may contain oxygen, hydrogen, nitrogen, and other gases in the compressed state; carbon dioxide, ammonia, chlorine, hydrogen sulphide, and other gases in the liquefied state; and acetylene in the dissolved state. Acetylene bottles are filled with porous charcoal and a solvent (acetone).

3. Bottles containing liquefied and dissolved gases are especially dangerous because they may burst at lower temperature as compared to compressed gas bottles.

4. The causes of gas bottle explosion may be:

(a) increase in the bottle pressure under the effect of heat (open flame, thermal radiation, solar radiation);

(b) concussion of bottles against hard objects;

(c) contamination of oxygen bottle nipples with greases, oils, and other organic substances.

Gas bottles must be kept at a distance of one metre from radiators and one and a half metres from burners and electric heaters, protected against solar radiation, and strapped against falling.

5. Keep large bottles outside the laboratory in cabinets with doors. In this case, the gas is supplied into the laboratory through pipes with a pressure regulator, the metal pipes being rated at high pressure.

6. Do not keep together bottles with hydrogen, chlorine, oxygen, and combustible gases. Keep bottles with chlorine, phosgene, hydrogen sulphide, and other toxic gases in specially provided rooms with powerful exhaust ventilation.

7. Tap gas from its bottle only through a pressure regulator meant exclusively for the gas in question and painted accordingly for identification. Send the pressure regulator gauges for testing at least once a year. Set the safety valve of the pressure regulator (low pressure chamber) at the maximum working pressure of the vessel into which the gas is fed.

8. After a compressed gas bottle has been used, the residual pressure in it must be at least $1 \cdot 10^5$ Pa.

9. When opening the valve of a bottle, do not use wrenches and other tools. If the use of a wrench is inevitable, do not press too hard for it may tear off the handwheel of the valve or damage the valve thread in the bottle neck.

XII. Fire Precautions

1. If a large amount of highly inflammable liquid is spilled, (a) immediately put out all burners and de-energize the electric heaters; (b) close the door, open the air vents and windows; (c) collect the spilt liquid using a towel or

a rag, wring the latter out over a wide vessel, and decant the liquid into a flask having a stopper; (d) stop airing the room only after the smell of the spilt liquid completely disappears from the room.

2. If a combustible liquid catches fire:

(a) switch off the heaters and burners;

(b) remove the combustible substances and materials lying nearby;

(c) cover the flame by a blanket or pour sand on it; if these measures are not sufficient, use a CO_2 fire extinguisher. Alcohols and other combustible liquids soluble in water may be extinguished by water. Foam fire extinguishers are not suitable for alcohols.

3. Extinguish burning phosphorus and alkali metals by sand or an asbestos blanket.

4. If wiring catches fire, first de-energize it, then use a foam fire extinguisher.

5. If your garments catch fire:

(a) do not run;

(b) put out the fire by wrapping yourself in a blanket, overcoat, etc.; do not use a fire extinguisher;

(c) if somebody with burning garments starts to run without letting others to put out the fire, catch him or her and do it.

6. All laboratories must be provided with dry sand, scoops, blankets, and fire extinguishers. The fire-fighting implements must be in good order and kept in a conspicuous and easily accessible place.

Do not block access to the fire-fighting implements and water taps.

7. In case of fire, immediately telephone the fire department and start putting out the fire by the available means before the firemen arrive.

XIII. First Aid Procedures

1. In the case of a chemical burn, immediately wash the affected area with a large amount of water and treat it with alcohol; when the burn is thermal, apply alcohol lavishly on the affected area and call a doctor without delay.

2. If the eyes are attacked by a chemical, immediately wash them with large quantities of water and go to the medical station.

3. If a solid particle gets in the eyes, call a doctor at once, do not rub the eyes, and do not try to remove the solid particle unaided to avoid complications:

4. In the case of intoxication with chemicals, immediately call a doctor and start rendering first aid. If the intoxication is caused by inhalation of toxic vapours or gases, take the affected person out to breathe some fresh air. If the intoxication is internal, make the affected person to vomit and give him or her an antidote. If necessary, apply artificial respiration (never do it when the intoxication is caused by chlorine, phosgene, and some other gases).

5. When handling a toxic substance or its components, make sure that you know well the first aid procedures, are able to render it, and have all the necessary medicines (antidotes) in the first-aid kit.

XIV. Special Rules

Handle autoclaves, gas bottles, and other pressure vessels in compliance with special instructions.

Handle sealed glass tubes, centrifuges, explosive, toxic and radioactive substances only with strict observance of the detailed instructions supplied by the instructor.

Table 1

First Aid Procedures

Injury	Procedure	Remarks
Burns: by fire, steam, hot objects: (a) first degree (redness)	Apply cotton soaked in ethanol. Repeat the procedure.	When the affected area is large, call a doctor
(b) second degree (blisters)	Ditto. Treat the burn with a 3-5% solution of potassium permanganate or a 5% solution of tannin.	Ditto
(c) third degree (destruction of tissue)	Apply a sterile bandage to the wound and call a doctor.	Ditto
by acids (sulphuric, nitric, phosphoric)	Wash the burn lavishly with water, then with a 5% solution of sodium bicarbonate.	Ditto
by alkalis	Wash the burn lavishly with water. If the eyes are affected, wash them with water. In the case of acid burns, wash them with a 3% solution of sodium bicarbonate. If the burns are caused by alkalis, use a 2% solution of boric acid.	Ditto
Intoxication: with aldehydes	Make the affected person drink a glass of a 0.2% solution of ammonia, then a glass of milk.	Call a doctor in any case
with ammonia	Make the affected person drink a large amount of water with vinegar or lemon juice to induce vomiting. Give him or her vegetable oil, milk, or egg white. In the case of ammonia inhalation, take the affected person out to breathe fresh air and allow him or her to rest.	Ditto
with aniline	When aniline is ingested, make the affected person to vomit and give him or her a laxative (salts). Do not give alcohol and vegetable oils. Let him or her inhale oxygen. Apply artificial respiration. If ammonia has affected the respiratory tracts, take him or her out to breathe fresh air; total rest, inhalation of oxygen; cardiac stimulants; camphor, caffeine.	Ditto
with barium salts	Induce vomiting and give a laxative (salts).	Ditto
with benzene	Same treatment as in the case of aniline.	Ditto

Table 1 (continued)

Injury	Procedure	Remarks
with iodine	Induce vomiting, give a 1% solution of sodium hyposulphite, starch paste, and milk.	Ditto
with carbolic acid (phenol)	Induce vomiting. Give a large amount of water, limewater, or a sugar lime solution (up to 20 g). As an alternative, give a table spoon of a suspension of magnesia (75 g) in water (500 cm³) every 5 min. Also give a diluted aqueous solution of potassium permanganate (1 : 4000).	Ditto
with acids	Rinse the mouth with water or a 5% solution of sodium bicarbonate. Give milk, a suspension of magnesia (10 g) in water (150 cm³), limewater, vagetable oil, and watery dough.	Ditto
with arsenic and antimony	Induce vomiting and give a laxative. Administer a teaspoon of the following antidote every 10 min (for arsenic): 100 g of ferric sulphate dissolved in 300 cm³ plus a suspension of magnesia (20 g) in water (300 cm³). Better results will be obtained by giving a flask of a freshly prepared Strzhizhevsky antidote: 1.25 g of sodium bicarbonate, 0.1 g of sodium hydroxide, 0.38 g of magnesium sulphate, and 0.5 to 0.7 g of hydrogen sulphide per 100 cm³ of solution.	Ditto
with hydrogen arsenide	Rest, inhalation of oxygen.	Ditto
with narcotics (ether, chloroform, soporifics, etc.)	Give 0.03 g of phenamine, or 0.1 g. of Corazol, or 30 drops of cordiamin, or 0.5 g of camphor. Give strong tea or coffee. Artificial respiration, inhalation of oxygen.	Ditto
with nitro compounds	Induce vomiting. Give a laxative (salts). Do not give alcohol, fats, and vegetable oils.	Ditto
with nitrogen oxides and nitric acid vapours	Rest. Give 2 g of norsulphazole, sulphazole, sulphazine, or sulphidine. Inhalation of oxygen.	Ditto
with carbon monoxide, ethylene, acetylene, lighting gas	Fresh air. Inhalation of oxygen or carbogen (a mixture of O_2 with 6% CO_2); artificial respiration.	Ditto
with tin compounds	Induce vomiting. Give a water suspension of magnesia and vegetable oil.	Ditto

Table 1 (continued)

Injury	Procedure	Remarks
with pyridine	Give a lot of tea or coffee. Artificial respiration.	Ditto
with mercury compounds	Give three fresh eggs with milk (about 1 liter). Induce vomiting. It is better to give a freshly prepared Strzhizhevsky antidote (see arsenic).	Ditto
with lead compounds	Give a large amount of magnesium sulphate.	Ditto
with silver compounds	Give a large amount of a sodium chloride solution or Strzhizhevsky antidote (see arsenic).	Ditto
with hydrogen sulphide	Give oxygen and apply artificial respiration at the same time	Ditto
with phosgene	Rest. Inhalation of oxygen.	Ditto
with phosphorus	Give 200 cm^3 of a 0.2% aqueous solution of $CuSO_4$. Do not give fats and vegetable oils.	Ditto
with sodium fluoride	Give limewater or a diluted (2%) solution of calcium chloride.	Ditto
with chlorine, bromine	Rinse the mouth with a 3% solution of sodium bicarbonate and a water suspension of magnesia. Give milk and a suspension of 10 g of magnesia in 150 cm^3 of water. Rest. Inhalation of oxygen.	Ditto
with hydrocyanic acid and its salts	Give a 1% solution of sodium thiosulphate or a 0.025% solution of potassium permanganate alkalized with sodium bicarbonate. Induce vomiting. Give up to 0.5 cm^3 (i. e., up to 10 drops) of amyl nitrite to be inhaled from a wad of cotton. Artificial respiration.	Ditto
with zinc compounds	Induce vomiting. Give egg in milk or Strzhizhevsky antidote (see arsenic)	Ditto
oxalic acid	Induce vomiting. Give milk of lime, castor oil	
Injuries: small cuts	Clean the wound mechanically, using sterile gauze. Dab the wound surface with a 3.5% iodine tincture. Wash the wound with water and soap, powder it with sulphanilamide or another sulphamide preparation, and apply sterile gauze and bandage.	Call a doctor
deep cuts with profuse hemorrhage	Apply a tourniquet above the wound, cover it with sterile gauze, and call a doctor.	Call a doctor

Table 2

Temperature of Ignition of Gases in Air

Gas	Temperature*, °C	Gas	Temperature*, °C
Methane	600-800	Carbon monoxide	630-650
Ethane	530-570	Hydrogen sulphide	300-400
Propane	530-570	Ethylene	520-540
Butane	500-550	Coke-oven gas	640-650
Acetylene	400-450	Hydrogen	...
Benzene	600		

* The exact ignition temperature in this range depends on the gas concentration.

Table 3

Explosive Ranges of Gases and Vapours

Gas	Explosive range of gas mixed with air, %		Gas	Explosive range of gas mixed with air, %	
	lower limit	upper limit		lower limit	upper limit
Hydrogen	4.1	75.0	Ethylene	3.0	16.0
Carbon monoxide	12.5	75.0	Acetylene	2.3	82.0
Methane	5.3	15.0	Hydrogen sulphide	4.3	45.5
Ethane	3.2	12.5	Ammonia	15.7	27.4
Propane	2.4	9.5	Coke-oven gas	5.6	31.0

Table 4

Cochran's Test Values ($P = 0.95$)

No.	$f' = m - 1$							
	1	2	3	4	5	6	7	8
2	0.999	0.975	0.939	0.906	0.877	0.853	0.833	0.816
3	0.967	0.871	0.798	0.746	0.707	0.677	0.653	0.633
4	0.907	0.768	0.684	0.629	0.590	0.560	0.637	0.518
5	0.841	0.684	0.598	0.544	0.507	0.478	0.456	0.439
6	0.781	0.616	0.532	0.480	0.445	0.418	0.398	0.382
7	0.727	0.561	0.480	0.431	0.397	0.373	0.354	0.338
8	0.680	0.516	0.438	0.391	0.360	0.336	0.319	0.304

Table 4 (continued)

No.	$f' = m - 1$							
	1	2	3	4	5	6	7	8
9	0.639	0.478	0.403	0.358	0.329	0.307	0.290	0.227
10	0.602	0.445	0.373	0.331	0.303	0.282	0.267	0.254
12	0.541	0.392	0.326	0.288	0.262	0.244	0.230	0.219
15	0.471	0.335	0.276	0.242	0.220	0.203	0.191	0.182
20	0.389	0.271	0.221	0.192	0.174	0.160	0.150	0.142

Table 5

Student t Test Values ($P = 0.95$)

f	t	f	t	f	t	f	t
1	12.71	6	2.45	11	2.20	16	2.12
2	4.30	7	2.36	12	2.18	17	2.11
3	3.18	8	2.31	13	2.16	18	2.10
4	2.78	9	2.26	14	2.14	19	2.09
5	2.57	10	2.23	15	2.13	20	2.09

Table 6

Fisher Test Values ($P = 0.95$)

Number of degrees of freedom	Number of degrees of freedom							
	1	2	3	4	5	6	7	8
1	161.45	199.50	215.71	224.58	230.16	233.99	236.77	238.88
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.24
10	4.97	4.10	3.71	3.48	3.33	3.22	3.14	3.07
11	4.84	3.98	3.59	3.36	3.20	3.10	3.01	2.95
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59
17	4.45	3.59	3.20	2.97	2.81	2.70	2.61	2.55
18	4.41	3.56	3.16	2.93	2.77	2.66	2.58	2.51
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45

Units of Measurement

| *SI System* | *Metric (non-sistem) Units* |

1. Units of Length

metre (m)	metre (m)
micrometre, $\mu m = 10^{-6}$ m	1 micron (μ)
nanometre, $nm = 10^{-10}$ m	1 angstrom $(\mathring{A}) = 10$ nm

2. Units of Volume

cubic decimetre (dm^3)	1 litre (l) = 1.000028 dm^3
cubic centimetre (cm^3)	1 millilitre (ml) = 1.000028 cm^3

3. Units of Mass

kilogramme (kg)	1 tonne (t) = 10^3 kg

4. Units of Force

newton (N)	1 kilogramme-force (kgf) = 9.80665 N
	1 tonne-force (tf) = 9806.65 N

5. Units of Work and Energy

joule (J)	1 kilogramme-force-metre (kgf·m) = = 9.80665 J
kilojoule (kJ)	1 erg (erg) = 10^{-7} J
	1 watt-hour (W·h) = 3600 J
	1 kilowatt-hour (kW·h) = $3.6 \cdot 10^6$ J
	1 calorie (cal) = 4.1868 J

6. Units of Pressure (Stress)

newton per square metre (pascal) $(N/m^2 = Pa)$	1 bar (bar) = 10^5 Pa
	1 dyne/cm^2 = 0.1 N/m^2 = Pa
	1 kg/cm^2 = 98066.5 N/m^2 = Pa
	1 mm H_2O = 9.8065 Pa
	1 mm Hg = 133.322 Pa
	1 atmosphere (atm) = = 101 325 N/m^2 = Pa

7. Units of Power

watt (W)	1 kg·m/s = 9.80665 W
	1 erg/s = 10^{-7} W
	1 horse power (h.p.) = 735.499 W
	1 kcal/h = 1.163 W
	1 kcal/s = 4.1868 W

8. Units of Dynamic Viscosity

newton per second per square metre $(N·s/m^2)$	1 poise (P) = 0.1 $N·s/m^2$
	1 centipoise (cP) = 10^{-3} $N·s/m^2$
	1 kg·s/m^2 = 9.80665 $N·s/m^2$

9. Units of Kinematic Viscosity

cm^2/s = 10^{-4} m^2/s	1 stoke (St) = 1 cm^2/s = 10^{-4} m^2/s
	1 centistoke (cSt) = 10^{-6} m^2/s

10. Units of Density

kg/m³

$$\left.\begin{array}{l} 1 \ \text{t/m}^3 \\ 1 \ \text{kg/dm}^3 \\ 1 \ \text{g/cm}^3 \end{array}\right\} = 1000 \ \text{kg/m}^3$$

$$\left.\begin{array}{l} 1 \ \text{kg/l} \\ 1 \ \text{g/ml} \end{array}\right\} = 999.979 \ \text{kg/m}^3$$

11. Units of Flow Rate

kg/s

$1 \ \text{kg/h} = 278 \cdot 10^{-6} \ \text{kg/s}$
$1 \ \text{kg/min} = 16.67 \cdot 10^{-3} \ \text{kg/s}$

12. Units of Space Velocity

m³/s

$1 \ \text{m}^3/\text{h} = 278 \cdot 10^{-6} \ \text{m}^3/\text{s}$
$1 \ \text{l/h} = 278 \cdot 10^{-9} \ \text{m}^3/\text{s}$
$1 \ \text{l/min} = 16.67 \cdot 10^{-6} \ \text{m}^3/\text{s}$
$1 \ \text{dm}^3/\text{s} = 10^{-3} \ \text{m}^3/\text{s}$

13. Units of Temperature

kelvin, K

$°\text{C}; \ T = t + 273.15$
$°\text{C} = T - 273.15$

14. Units of Specific Heat

J/kg·deg = 10^{-3} kJ/kg·deg

J/m³·deg = 10^{-3} kJ/m³·deg

$1 \ \text{cal/g} \cdot \text{deg} = 4186.8 \ \text{J/(kg} \cdot \text{deg})$
$1 \ \text{kcal/kg} \cdot \text{deg} = 4.1868 \ \text{J/(kg} \cdot \text{deg})$
$1 \ \text{kcal/m}^3 \cdot \text{deg} = 4186.8 \ \text{J/(m}^3 \cdot \text{deg})$